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APRIL 1958

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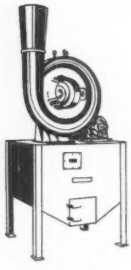

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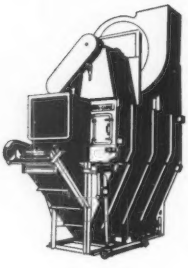

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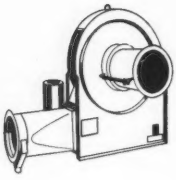

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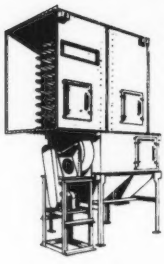

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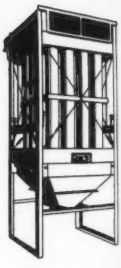

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The Control of a Lead Hazard in the Silversmithing Industry

LEONARD D. PAGNOTTO

Assistant Chemist, Massachusetts Department of Labor and Industries

HAROLD BAVLEY

Senior Engineer, Massachusetts Department of Labor and Industries

COMPETITION in the manufacture of products for which there is a popular demand often necessitates the replacement of an expensive, innocuous material by one that is less costly but highly toxic. This substitution has occurred in the silversmithing industry, where lead has replaced the more expensive tin in Brittania metal used for the production of parts of silver-plated holloware.

The introduction of small quantities of lead into the alloy was gradual at first, but economy eventually dictated the need for larger quantities of the less expensive material, so that the base metal now contains up to eighty-six per cent of this toxic substitute.

The well-deserved respect for the toxicity of this metal, earned during its many years of use by industry, has manifested itself in the requirement for suitable engineering and medical controls to prevent lead intoxication. The silversmithing industry has not been an exception and has provided such controls at the obviously hazardous operations of melting, casting, soldering, brazing, and grinding. However the hazardous sequelae, resulting from the use of lead during its gradual introduction, were not fully recognized in a special, but frequently used, metal-burnishing operation, called, in this industry, "sandbobbing."

The sandbobbing operation is performed usually prior to the cleaning and final polishing of the holloware parts. A layered rag or walrus hide wheel, mounted on a lathe mandrel, is located in front of a box-like housing situated on the worktable. The abrasive used is pumice, which has been moistened lightly with mineral oil. The bulk of the abrasive is stored within the work booth. As needed, the worker applies the abrasive to the part to be sandbobbed immediately prior to the actual contact of the piece with the wheel. Abrasive and metallic dusts are thrown off the periphery of the wheel by its rotating action. Usually the worker's clothes, face, hands, and the surrounding work areas become covered by this dust. The abrasive is presumably changed at least once a week.

An employee of one of the silversmithing plants engaged in the manufacture of holloware became ill while working at this sandbobbing operation and sought medical advice from his family physician. During his treatment the worker remained away from his job, and hence from any exposure to lead for a period of three weeks, but even after this time lapse an analysis of his urine revealed that he was still excreting an amount of lead considered to be indicative of a previous hazardous exposure. The urinalysis further revealed a correspondingly elevated coproporphyrin excretion indicative of body dysfunction.

A visit was made to the worker's place of employment to survey his job environment in an effort to determine how the sandbobbing operation contributed to his illness. Determination of the atmospheric contamination was made at the breathing zone of several operators similarly engaged in sandbobbing at this plant. In all cases, the values were found to exceed the maximum allowable atmospheric concentration for lead permissible in the Commonwealth of Massachusetts. These excessive atmospheric lead values prompted a similar survey of several major silversmithing shops in Massachusetts. Atmospheric samples were obtained to determine the extent of contamination during the performance of this operation. The lead absorption by the sandbobbers was determined by urinalyses. The atmospheric and urinalyses results indicated the need for engineering control of the sandbobbing operation.

Samples of the contaminated abrasive, which were obtained at these plants and which had been used for varying lengths of time, showed contamination of the pumice with particles of the lead-base alloy. The extent of contamination was found to be dependent upon the amount of sandbobbing performed. The range of lead contamination varied from 3.2 per cent for

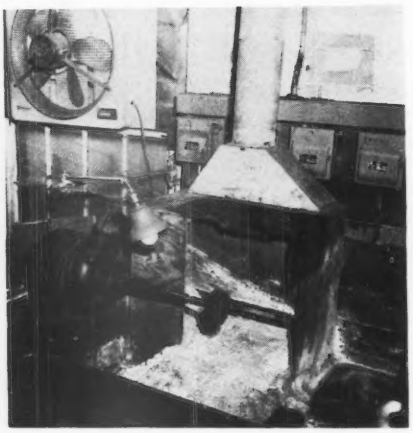


FIGURE 1. View of sand-bobbing work booth with wheel guard removed, showing salvage baffle

The proper control of the lead dust dispersion necessitated the design of a "tailored" exhaust-ventilated work booth. A model booth was constructed in the sandbobbing department of one of the silversmithing shops to determine the most effective method of controlling the dust dispersion without interfering with the worker's method of operation. An engineering drawing specifying the airflow and control velocity requirements, and illustrating the proper arrangement of the essential wheel deflector guard and the abrasive salvage baffle, was submitted to the management of each surveyed silversmithing shop. It was found that in most cases ventilation could be effectively provided by connecting the new work booths to an existing installation. Recommendations for improved personal hygiene were discussed with the workers and the shop supervisors.

Satisfactory cooperation was obtained from management in the construction and installation of the ventilated booths, and the institution of proper hygienic practices. Subsequent atmospheric sampling and urinalyses revealed that the control recommendations had resulted in a dramatic reduction in the workroom atmospheric contamination, with a correspondingly substantial reduction in lead absorption. In addition, the control of the dust dispersion resulted in an improvement in the workers' appearance. The accumulation of settled dust in the work areas became minimal, resulting in a reduction in the amount of janitorial service previously required.

TABLE I

Urine Analyses*

Before Ventilation					After Ventilation				
Mg. of Lead per Liter of Urine		No. of Tests	Mg. of Coproporphyrin Per Liter of Urine		Mg. of Lead per Liter of Urine		No. of Tests	Mg. of Coproporphyrin Per Liter of Urine	
Range	Average		Range	Average	Range	Average		Range	Average
0.10–0.67	0.23	30	.10–4.4	1.5	.07–.17	0.10	15	.2–1.1	..4

* Urine samples adjusted to a mean specific gravity of 1.024.

Urinary lead and coproporphyrin excretion of sandbobbers before and after instituting engineering control.

TABLE II

Air Analyses

Before ventilation			After ventilation		
No. of Tests	Mg. of Lead per 10 Cubic Meters of Air		No. of Tests	Mg. of Lead per 10 Cubic Meters of Air	
	Range	Average		Range	Average
15	1.00–17.00	6.00	8	0.10–.40	.25

Maximum Allowable Concentration 2.0.

Atmospheric Lead values found before and after ventilation of sandbobbing stations.

pumice used half a workday to 8.5 per cent for the abrasive used approximately one week.

Additional cases of lead intoxication occurred prior to the termination of the survey, pointing up the necessity for proper control as soon as feasible, to prevent other incidents of lead intoxication.

Summary

A lead exposure hazard in a metal-burnishing operation, peculiar to the silversmithing industry, was investigated and subsequently controlled by instituting effective engineering and hygienic measures.

Instrument Developments in Health Physics*

F. E. ADLEY

Industrial Hygiene Operation, General Electric Company, Richland, Washington

The performance characteristics and construction features are described for several instruments that were developed for specific applications in industrial hygiene in the nuclear energy industry. Two monitors, an automatic particle sampler and an NO_2 recorder, are discussed. An apparatus for testing respirator performance is shown. A reciprocating attachment for the random collection of particles by electrical precipitation is mentioned. Also reviewed are a microscope attachment for locating radioactive particles and a device for increasing the rapidity of manually measuring particle sizes from microprojections. Photographs are included.

HEALTH PHYSICS evaluations in the nuclear energy industry are usually based on or derived from measurements made by some form of instrumentation. In many instances existing instrumentation and techniques have been adopted from allied fields. However, novel situations have arisen which required the development of improved methods to solve the problems peculiar to this industry.

One group of instruments comprises those designed for the appraisal of problems related to inhalation or atmospheric contamination. This resumé is confined to this group and describes the significant features of several instruments or devices that were built and proven useful at Hanford over the last several years.

Particle Monitor

The first instrument is an automatic particle sampler, designed primarily for the sampling of radioactive particulates from stacks, although it can be used also for environmental sampling. The primary objective was to obtain a continuous series of interval samples that would permit subsequent analysis by direct counting, ashing or digestion followed by radiochemistry or autoradiography. It was essential that there should be minimal or no leakage of the highly contaminated atmospheres to the cabinet interior during operation as this would complicate servicing.

This monitor (Figure 1) was built several years ago and has given satisfactory performance. Since the original model was constructed, several others have been developed that include a number of refinements such as built-in counting equipment and continuous moving tapes.

In operation, the air sample enters through line "A" and is drawn through the strip filter paper "B", the type of which is determined by the application or use involved. After a sampling interval, the pump stops and solenoid "C" closes a valve to prevent any flow of contaminated gas during the filter change and sampling head "D" opens to permit the filter tape to be moved by the power spool "E". The tape, which has a hole made by punch "F" during the previous sampling period, moves until the hole is aligned with a light source and a photocell "G". The tape then stops and the components are actuated for the next sampling cycle. Sampling periods may be varied from one minute to 20 hours. Since some volatile fission product may be retained on the tape, a strip heater "H" maintains a sufficiently elevated cabinet temperature to volatize this contaminant. The vaporized products are removed directly by a small canopy-type hood "J" over the tape. Replacement air for this hood enters through a respirator filter cartridge "K" which ensures a clean cabinet atmosphere.

In some instances Millipore filters have been superimposed along the tape to collect samples. Such samples can be assayed by any of the various ways possible with this filter. They can be counted directly, analyzed chemically, autoradiographed, or subjected to light or electron microscopy.

Nitrogen Dioxide Monitor

Nitrogen dioxide is an air contaminant commonly associated with industrial operations and its presence frequently creates a need for air sampling to determine the concentrations present. To indicate the fluctuations and peak con-

* Work performed under Contract No. W-31-109-Eng-52 between the Atomic Energy Commission and General Electric Company.

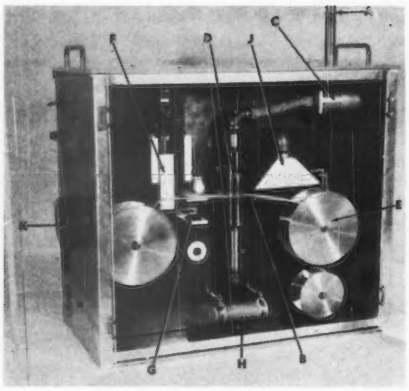


FIGURE 1

centrations of NO_2, a continuous monitor was built for use in stack and environmental sampling. This portable instrument, shown schematically in Figure 2, has a range from about 0.50 ppm to 15,000 ppm NO_2.

In addition to recording stack emissions, the instrument can be applied to the evaluation of workers' exposures at operations such as metal pickling, metal dissolving and welding. Another application is to measure the concentration and duration of the ground contact of stack gases as related to meteorological parameters. In such cases the presence or passage of contamination can be timed to less than one minute.

During operation, the air sample is drawn down through a beaded column in concurrent flow with the reagent, which consists of tartaric acid, sulfanylamide and N - 1 naphthylethylenediamine dihydrochloride. A colorimetric reaction occurs which is detected in a flow-through colorimeter. The change in light transmission is recorded on an Esterline-Angus recorder calibrated in ppm of NO_2.

Reciprocating Electric Precipitation Collector

Electrostatic precipitation has been utilized for many years for the collection of airborne particulate specimens for qualitative and quantitative analyses. The application of this technique for the collection of specimens for particle size analyses by light and electron microscopy indicated the need for more representative particle deposition. The various forces acting on a particle in an electrostatic field are known to influence the deposition pattern of the specimen, depending on the particle sizes involved. For this reason an electron microscope screen placed at any location in the collection field would have a biased particle size distribution. Consequently, to minimize this difficulty, an attachment was devised, as shown in Figure 3, for the familiar type of electric precipitator air sampling head.

Bar "A", six inches long and having a 1/8 inch square cross section fits into a longitudinal slot in the collection tube so that the inside surfaces of the bar and tube are flush. A cylindrical cam "B", driven by a telechron motor, causes the bar to reciprocate at a uniform speed once each minute. Electron microscopy specimen screens are mounted on the bar so that they completely traverse the collection zone. Specimens obtained with this attachment have been found to contain representative, random distributions of particulates.

Microscopy of Radioactive Particles

In the study of particle specimens there occasionally arises the need to distinguish or isolate a few radioactive particles from a gross specimen containing many inert particles. In most instances it is impossible to visually distinguish the radioactive particles from those which are inert. To accomplish the task, a microscope attachment was made which utilized the radioactive property of the particles to effect their differentiation. This accessory, which was termed a "collimating" attachment, is shown in Figure 4.

The device consists of a brass plate machined to fit under the microscope stage, replacing the substage condenser. The plate embodies a conical aperture with a #80 drill hole at the apex. This hole has an area of about 0.09 mm^2. A scintillation crystal sealed on the top of a photomultiplier tube is mounted flush with the bottom of the conical aperture. The tube is connected through an amplifier to an audible signal. To determine which particle in a field is radioactive, the specimen slide is traversed over the hole until the signal indicates that a radioactive particle is over the hole. By successively moving the slide in several directions it is possible to orient the particle that is radioactive. Oblique overstage illumination is used in this system.

Scalomatic

Another instrument related to particle size determinations was devised for the measurement of a series of individual particles to obtain their size distribution. This instrument, termed a Scalomatic, is shown in Figure 5.

Images of particles from microprojections can be measured by means of this instrument. The

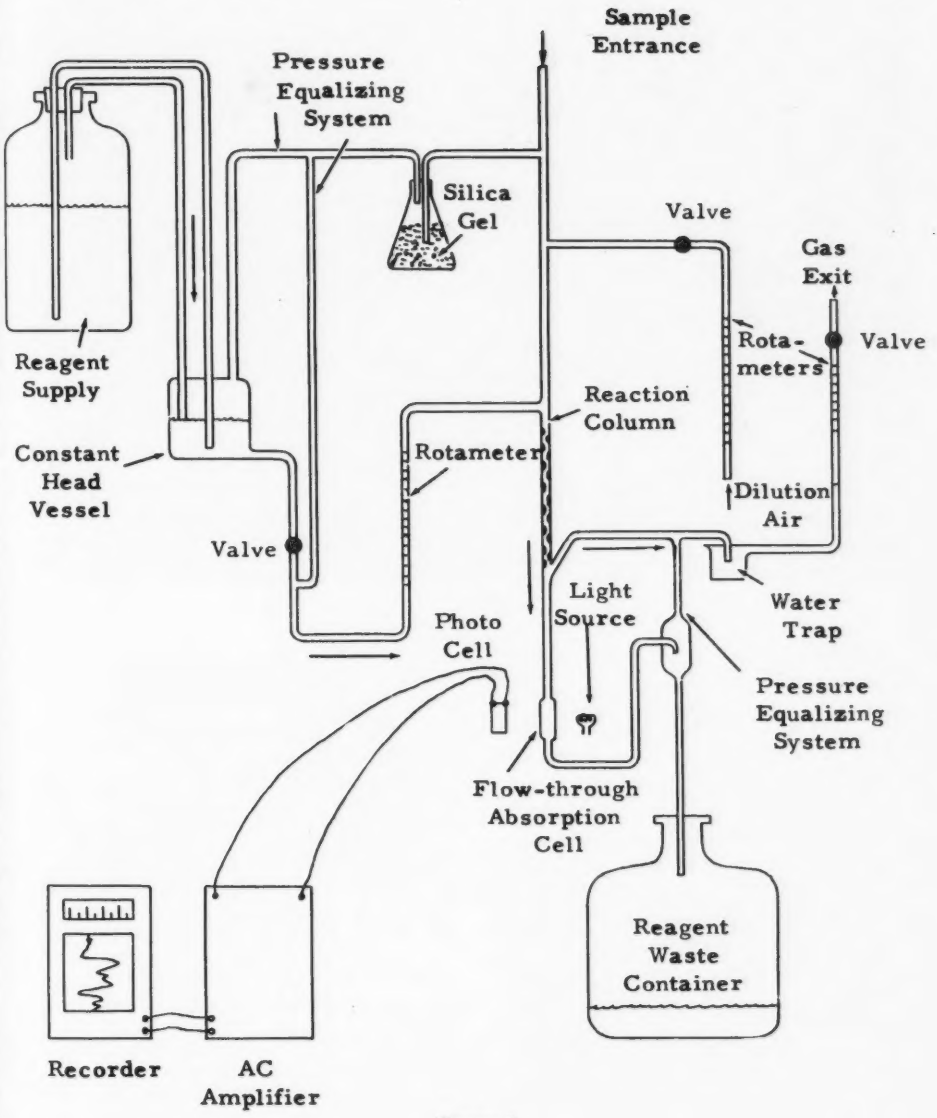


FIGURE 2

calipers, lower left in Figure 5, are conventional in shape except that the legs are extended through the pivotal point to an arc-shaped strip containing a continuous series of electrical contact strips. Each of these contact segments is wired to a solenoid that actuates one of a bank of tally-counters. One leg is fixed to the electrical strip; the other contains a wiper contact that positions itself according to the setting of the calipers. At any position, a foot switch can be closed, thus registering a tally for that position or image size. To measure and record the image size it is necessary only to span the particle image with the calipers and press the foot switch.

Several calipers are available, each containing a different number of contact segments. Those with many segments produce a more detailed

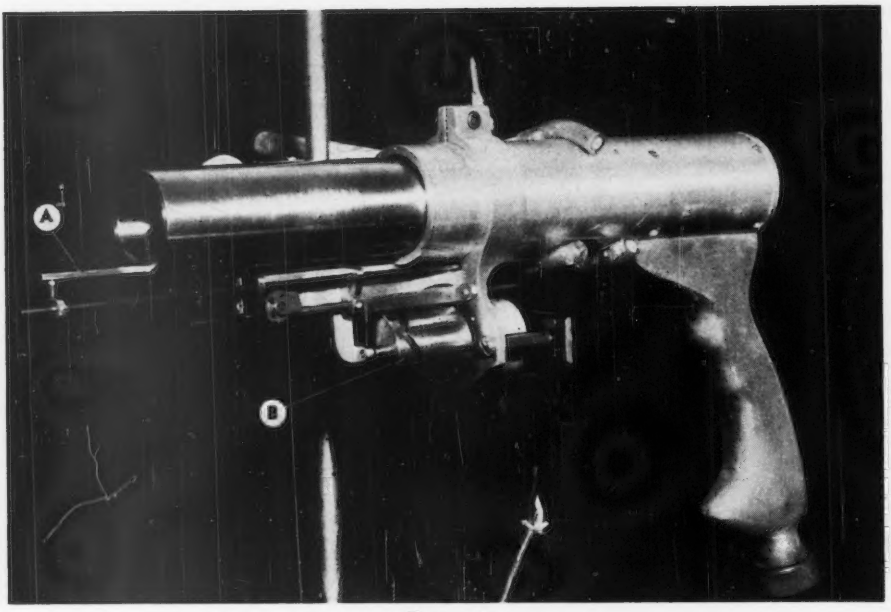
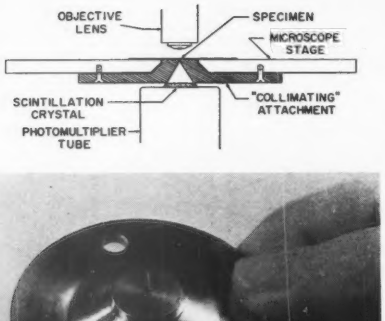


FIGURE 3



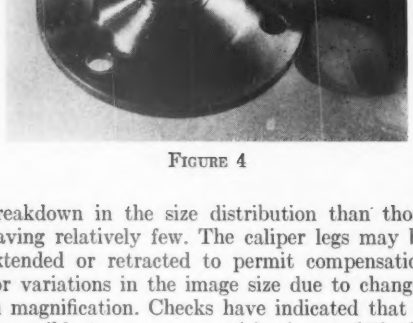


FIGURE 4

breakdown in the size distribution than those having relatively few. The caliper legs may be extended or retracted to permit compensation for variations in the image size due to changes in magnification. Checks have indicated that it is possible to measure particles in one-fifth the time usually required by manual methods and is much less tedious.

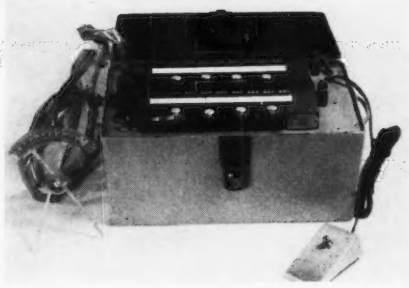


FIGURE 5

Respirator Tester

The final piece of equipment in this review is a respirator testing apparatus that has proved very useful in radiological protection at Hanford. Since there was a decided gap in the knowledge of the performance of respirators being used, a testing device was constructed that measured filter efficiencies, leakage caused by the fit of the facepiece and indicated some of the characteristics of the individual respirators. This apparatus is shown in Figure 6.

The tester has the side panels removed to show the mechanism. The breather pump system was designed to closely simulate human respiration to demonstrate any reduction of pro-

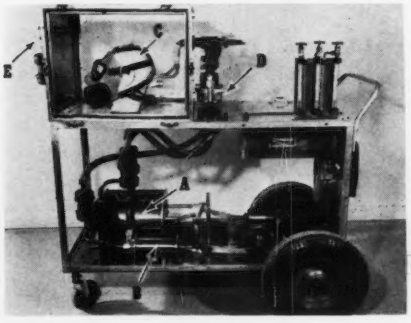


FIGURE 6

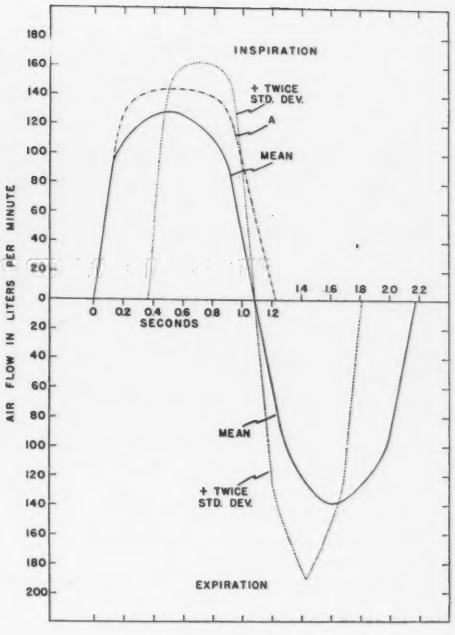

INSPIRATION
+ TWICE STD. DEV.
A
MEAN
MEAN
+ TWICE STD. DEV.
EXPIRATION
AIR FLOW IN LITERS PER MINUTE
SECONDS
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2
180 160 140 120 100 80 60 40 20 0 20 40 60 80 100 120 140 160 180 200

FIGURE 7

tection that might be caused by the pulsations due to inhalation and exhalation. The respiration rate is 29 per minute and the maximum inspiratory airflow rate is about 160 liters per minute, which conform with respiratory conditions caused by light work. These requirements approximate those from Silverman's[1] findings in his work on breathing rate studies. Figure 7 is a graphical representation of Silverman's results showing average inspiratory airflow rates.

Since the airflow rates of a simple plunger pump action produce a sinusoidal-shaped curve as contrasted with the dome-shaped curve from human respiration shown here, a system was devised whereby a large pump "A" was connected to a smaller pump "B" operating three times as fast. The resultant combined airflow, measured by kymographs, agreed well with the average human respiratory rates shown in Figure 7.

A respirator is tested by mounting it on a manikin head "C" built up of latex that has the resiliency and texture of human tissue. An inhalation tube passes from the mouth through the head and out the rear where a high-efficiency sampling filter "D" is located. Two exhalation tubes pass through the rear of the head to the nasal region. These tubes are connected to the breather pump manifolds. A second pumping system identical to the one just described, is used for sampling the chamber atmosphere concurrently with the respirator testing system. A synthetic test aerosol, such as NaCl fume, can be introduced into the chamber inlet, "E", or the apparatus can be moved to the site of a questionable atmosphere which may be either radioactive or inert. In the instance where an actual plant atmosphere is utilized it is drawn into the chamber, and the mask is tested, in situ.

The results obtained with this apparatus have proven useful in providing data for the establishment of mask limits so that each type of respiratory device can be used with greater understanding of its characteristics and limitations.

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1. SILVERMAN, L., et al.: "Fundamental Factors in the Design of Protective Respiratory Equipment, End Point Breathing Rate Studies," p. 81, August 1, 1944.

INDUSTRIAL HYGIENE POSITIONS

The Executive Secretary of the AMERICAN INDUSTRIAL HYGIENE ASSOCIATION maintains a list of positions in the field of industrial hygiene. Prospective employers and those seeking employment in industrial hygiene are encouraged to make use of this service. Inquiry should be directed to GEORGE CLAYTON, Executive Secretary, AIHA. 14125 Prevost, Detroit 27, Michigan.

Studies on the Toxicity of n-Propyl Nitrate Vapor*

WILLIAM E. RINEHART, ROBERT C. GARBERS, EARLE A. GREENE, and ROBERT M. STOUFER

Directorate of Medical Research, U. S. Army Chemical Warfare Laboratories, Army Chemical Center, Maryland

ESTERS of nitric acid and aliphatic alcohols are known to produce toxic effects.[1, 2, 3, 4] One of these esters, n-propyl nitrate, has been investigated[1, 2] for its pharmacologic effects in animals. Murtha, Stabile, and Wills[1] reported the material to have an approximate LD50 dose by intravenous injection of 225 mg./kg. in rabbits. They noted respiratory depression, cardiac effects, and a prompt hypotension, probably caused in part by direct action of the material on vascular smooth muscle. Hood[2] reported that the compound produces cyanosis, methemoglobinemia, and death in rats after inhalation of the vapor at approximately 10,000 ppm for four hours. A desire for information on the toxic effects produced by repeated exposure to n-propyl nitrate vapor prompted this laboratory to perform such a study.

Procedures

The n-propyl nitrate† was dispersed as a vapor in a 0.7 $m.^3$ dynamic gassing chamber by volatilizing it with dry nitrogen from heated bubblers; the vapor being mixed with room air in a mixing bowl prior to entry into the chamber. The chambers were operated at a flow rate of 0.2 m^3/min. Atmospheric samples from the chamber were collected in isopropanol and analyzed by a modification of the method of Yagoda,[6] substituting thymol for m-xylenol in a colorimetric determination of total nitrate.

Animals were exposed for a single 4 hour period or for repeated 6 hour periods for 5 days a week for a maximum of 6 months. Wistar strain rats, Carworth strain mice, golden hamsters, Hartley strain guinea pigs and male beagle dogs were used in the various exposure sequences. Additional rodents were exposed for periodic sacrifice and pathologic examination. Food and water were witheld from all rodents (exposed and control) during the 6 hour a day exposure periods.

Dogs were bled from the radial vein at selected time intervals for clinical laboratory studies. Hematocrit, prothrombin time and white blood cell counts were carried out by methods described by Wintrobe.[7] Hemoglobin was determined by measurement of oxyhemoglobin using the Klett-Summerson photoelectric colorimeter.[8] Methemoglobin was determined by the method of Evelyn and Malloy[9] and was expressed in per cent, as the ratio of methemoglobin to total hemoglobin. The blood non-protein nitrogen was measured by a micro-Kjeldahl method[10] and liver function was appraised by zinc turbidity tests after the method of Kunkel.[11]

Experimental Results

The clinical signs and mortality show by rodents exposed to the various concentrations are given in Table I. Toxic signs, such as cyanosis and lethargy in rats, and cyanosis and excitement and/or convulsions in mice were noted only during and shortly after exposure. All deaths in the single 4-hour exposure studies at 5816 and 7134 ppm occurred during exposure or within 16 hours following the exposure. There was no evidence of persistent cyanosis in surviving rodents from any concentration level on the morning following exposure. Hamsters and guinea pigs showed no toxic signs at any concentration studied. Rats, mice, and guinea pigs, which were repeatedly exposed, were weighed individually, as were their respective controls, at frequent intervals throughout the experimental series. There was a trend for the exposed rodents to gain weight at a slower rate than their respective controls. In one instance, i.e., rats exposed repeatedly to 3235 ppm for 6 hours a day for 8 weeks, there was a weight loss during the first week.

Dogs were found to be more sensitive to the

* Presented at the Eighteenth Annual Meeting of the AIHA, St. Louis, Mo., on April 26, 1957.

† The compound is a pale yellow liquid boiling at 110°C, has a sweet odor, a vapor pressure of about 16 mm of Hg at 25°C, and is insoluble in water but soluble in alcohol and ether (5). The n-propyl nitrate used for these studies was obtained from Ethyl Corporation. It was calculated to be 98% pure based on total nitrate present and contained less than 1% of nitrites.

TABLE I

Summary of Rodent Exposures to n-Propyl Nitrate

Conc. (ppm)	Duration of Exposure	Species	Clinical Signs	Mortality	
				Male	Female
7134	4 hrs.	Rats	Cyanosis, lethargy	1/5	0/5
		Mice	Cyanosis, convulsions	9/10	6/10
5816	4 hrs.	Rats	Cyanosis, lethargy	1/10	
		Mice	Cyanosis, convulsions		2/10
3235	8 wks.*	Rats	Lethargy, moderate cyanosis	5/20	
		Mice	Excitement, moderate cyanosis		6/29
		Hamsters	None	0/10	
		Guinea Pigs	None	0/10	
2110	26 wks.*	Rats	Lethargy	9/20	
		Guinea Pigs	None	0/10	

* 6 hours a day, 5 days a week repeated exposures.

TABLE II

Summary of Dog Exposures to n-Propyl Nitrate

Conc. (ppm)	Duration of Exposure	Clinical Signs	Mortality
2000	11 hrs.*	Cyanosis, methemoglobinemia, vomiting, convulsions, death.	3/3
900	6 days*	Cyanosis, methemoglobinemia, hemolytic anemia, hemoglobinuria, collapse, death after 6 days.	1/1
560	6 wks.*	Cyanosis, mild methemoglobinemia and hemolytic anemia, hemoglobinuria, depression for 2 weeks, death in 1 dog after 6 exposures.	1/2
260	26 wks.*	Hemoglobinuria, mild anemia, and slight depression for 2-3 weeks. Apparent complete recovery.	0/3

* 6 hours a day, 5 days a week repeated exposures.

TABLE III

Typical Clinical Laboratory Values on Dog Exposed to 900 ppm of n-Propyl Nitrate

Time of Bleeding	Hct %	$HgbO_2$ Gm. %	MeHgb	
			Gm. %	% of total
Pre-exposure	64	19.3	0.0	0.0
Post 2nd exposure	55	16.4	2.9	17.5
Pre 3rd exposure	51	15.4	2.2	14.2
Post 3rd exposure	50	14.6	4.6	31.7
Pre 4th exposure	39	12.2	3.0	24.3
Post 4th exposure	35	11.9	5.3	44.2
Pre 5th exposure	24	9.4	2.3	24.9
Post 5th exposure	22	8.6	2.6	20.0
Disposition of dog—death after 6 exposures				

effects of the vapor than were rodents. The clinical signs and mortality shown by dogs are given in Table II. The toxic signs of cyanosis, depression, and hemoglobinuria were persistent and progressed to greater severity from day to day in dogs exposed at 560 ppm or higher. At 2000 ppm, death occurred within 2 days for 3/3 dogs; at 900 ppm, death occurred on the first day following 6 exposures in 1/1 dogs; and at 560 ppm, death occurred after 6 exposures in 1/2 dogs, while the other dog survived 30 exposures. No deaths occurred from exposure to 260 ppm for 6 months. Hemoglobinuria was noted after the second or third exposure in surviving animals but disappeared after two weeks of continuous exposures. This effect as well as the apparent depression of the animals did not reappear during the prolonged experiments. Dogs which showed severe toxic signs were noted to have elevated rectal temperatures as high as 106°F prior to death.

Clinical laboratory tests on the blood of dogs exposed to high concentrations showed definite changes in hematocrit, oxyhemoglobin, and methemoglobin. At 900 ppm and higher, hematocrit and oxyhemoglobin values decreased continuously to death, whereas methemoglobin values increased from day to day with a slight overnight recovery. At 560 ppm, there was no accumulation of methemoglobin from day to day, although it was present in low concentrations, and the anemic condition reversed after two weeks. There were no changes other than an initial mild anemia due to exposure to 260 ppm for 26 weeks. All other clinical laboratory tests gave no evidence of any significant changes. Typical clinical laboratory values for two dogs exposed to 900 ppm and 560 ppm, are given in Tables III and IV, respectively.

Pathologic examination of tissue preparations from animals which succumbed to the higher exposure concentrations revealed changes typical of acute anoxia. Animals which were routinely sacrificed from the repeated exposure experiments showed a significant amount of pigment in the Kupffer cells of the liver and in the spleen of dogs and rodents, and occasional valvular edema and/or pigment deposition in the heart of rodents.

At a concentration of approximately 50 ppm, based on a theoretical calculation from chamber deequilibration, the material was noted by one of the authors (W.E.R.) to have a definite

TABLE IV

Typical Clinical Laboratory Values on Dog Exposed to 560 ppm of n-Propyl Nitrate

Time of Bleeding	Hct %	$HgbO_2$ Gm. %	MeHgb	
			Gm. %	% of total
Pre-exposure	49	14.0	0.0	0.0
3 days	34	9.4	0.1	1.0
6 days	24	6.5	0.1	1.5
9 days	32	8.6	0.1	1.2
16 days	40	10.2	—	—
26 days	41	10.6	0.1	0.9
30 days	43	11.5	0.2	1.7
Disposition of dog—survival and apparent complete recovery				

sickening sweet odor, and it produced a somewhat "light-headed" feeling.

Comments

The studies on n-propyl nitrate which have been reported here show that a considerable toxic effect may be developed from exposure to the vapor. For the species involved in these studies, more serious effects seemed to occur from single exposures at high concentration, i.e. 5000 ppm or above for rodents and 900 ppm and above for dogs, rather than from repeated exposures at lower concentrations. The main effect to rodents from inhalation of the vapor appears to be anoxia caused by a lowered oxygen content of the blood as a result of methemoglobin formation. The toxic effect on dogs is similar but more severe and resulted in a higher order of toxicity. The occurrence of hemoglobinuria and hemolytic anemia in the early stages of exposure together with the production of methemoglobin resulted in a much lower oxygen carrying capacity in dogs than in rodents, which did not develop anemia. Dogs exposed to 560 ppm for 6 weeks and to 260 ppm for 26 weeks were, however, apparently able to tolerate the anemic condition providing initial damage was not too severe. Blood level values returned to normal or near normal within two to three weeks even upon continued exposures to a particular concentration level. These dogs did not show an appreciable development of, nor an accumulation of methemoglobin from day to day continuous exposures as did dogs exposed to 900 ppm or higher.

Examination of tissues from the repeatedly exposed rodents or dogs did not show any pathologic damage. The only abnormal effect noted was an increase in pigment deposition in the liver and spleen. This effect may be ascribed to hemolysis and to increased hematopoietic activity during the course of the exposures.

At present, at least to the authors' knowledge, there is no information as to the quantitative susceptibility of man to the toxic effects of n-propyl nitrate vapor. Due to the great difference in level of toxicity for dogs and rodents, special caution should be exercised to prevent a severe exposure to man. If we assume that a man is at least as sensitive as a dog and shows a similar reaction to the material, there are certain conclusions which might be drawn. First, a mild anemia and/or hemoglobinuria without the formation of appreciable amounts of methemoglobin could be an indication of chronic exposure; second, the presence of both anemia and mild methemoglobinemia could be an indication of a fairly severe exposure of some duration; and third, large amounts of methemoglobin present in the blood would be evidence of a very severe exposure. These factors should be considered as possible indices of exposure for man. However, it has been noted that the odor of the material is fairly obvious and presumably is detectable at concentration levels of 50 ppm or above. The detection of this odor or any concentration resulting in discomfort to the worker in the form of irritation, headache, or nausea may be the real basis of evaluation of a safe and acceptable concentration level in the working atmosphere.

Consideration of the vapor pressure of n-propyl nitrate which was previously mentioned to be below that of water at 25°C would result in a theoretical saturation concentration of 21,000 ppm. Werner, Mitchell, Miller, and von Oettingen[12] stress the importance of comparison of materials on the basis of potential hazard rather than on toxicity alone. They define a hazard index as the ratio of the average concentration which could theoretically be present in a saturated atmosphere under standard conditions to the median lethal concentration. From our experiments with rodents, we can estimate the approximate 4-hour lethal concentration to be 9,000–10,000 ppm for rats, agreeing closely with Hood's[2] values; and 6000–7000 ppm for mice. These data would yield hazard indices of 2–3, or approximately the same potential hazard as aniline or furfuryl alcohol.[13] If we estimate a 4 hour lethal concentration for dogs from our data to be around 2000–2500 ppm, we calculate a hazard index of 8–10, or a four-fold increase in potential hazard.

A concentration of 260 ppm of n-propyl nitrate vapor, which was the lowest concentration studied in these experiments, caused slight clinical signs in dogs during the first two weeks

of exposure. A safety factor should be considered in extrapolating to man for establishment of a maximum acceptable concentration (MAC). It is the authors' opinion that a reasonable safe level of operation should be no higher than 50 ppm of the vapor, which is approximately ⅕ of the concentration which produced minimal toxic effects in dogs. Until further information on the susceptibility of man to n-propyl nitrate vapor becomes available, it is recommended that personnel exposed to concentrations around this level of 50 ppm be under medical observation.

Summary

The main toxic effects from inhalation of n-propyl nitrate vapor are methemoglobinemia and anoxia although dogs exposed repeatedly to sublethal concentrations also showed clinical laboratory evidence of hemolytic anemia and hemoglobinuria. Upon continued exposure, this anemic condition may be reversed by a compensatory increased hematopoietic activity. The vapor hazard of the material for rodents is similar to aniline or furfuryl alcohol, but dogs are considerably more sensitive to the toxic effects of the vapors. It may be found that man is of similar or greater sensitivity and a safe operational limit may have to be established on the basis of personal discomfort. A reasonable maximum acceptable concentration for man may be 50 ppm or less based on animal experimentation.

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Noise Exposure Evaluation

(Auditory Effects)

EDWARD W. POTH[1] and CARL J. WEINBERG[2]

For the past several years the Industrial Hygienist has been faced with the problem of measuring and evaluating a new or at least to some extent, a different kind of environmental hazard, namely noise. In many respects this hazard is no different from other hazards encountered in industrial health work. The cause and effect aspects are virtually the same for exposure to either hazardous noise or ionizing radiation. In both cases the time, intensity and nature of the radiations largely determines the extent of possible damage or injury to man. With ionizing radiation, we have a considerable background of experience, and have, over a period of some fifty years, developed numerous time-dose exposure relationships. These relationships define the hazard in terms of exposure to a certain number of roentgens, rems or rads per hr/wk/day, etc. Likewise, we have determined the relative damaging effects of the various types of ionizing energies. With sound, we measure the energy and determine the spectra with precise accuracy; however, our limited experience with noise exposure precludes the delineation of cause and effect with the same degree of assurance that we describe when dealing with ionizing radiation. For this reason we must at present depend on the best judgement of those individuals who have pioneered in the field of acoustics, and wait for the time when sufficient data is available to either substantiate or repudiate these judgements.

When most industrial health problems are evaluated by the Industrial Hygienist, benchmarks are available to indicate what action should be taken with regard to a specific hazard. These benchmarks, or guideposts, are expressed as Threshold Limit Values, or in the case of radiation, Maximum Permissible Activity. Unfortunately for the Industrial Hygienist, the pioneers in acoustics upon whose best judgements we now rely for these cause and effect relationships, have not expressed noise or sound values in this manner. Instead, we have damage risk criteria which indicate the constant maximum noise levels to which personnel may be continuously exposed during an 8 hour work day for a lifetime.[1] We also have the ASA Z24-X-2 subcommittee report[2] which, on the basis of trend curves, points out the relationship between continuous noise exposure and the probability of hearing loss. A recent WADC Tech Note[3] advocates the extension of criteria to include high intensity short time exposure. On the basis of the equal energy exposure concept, criteria for high intensity aircraft noise are presented for both the protected and unprotected ear.

These data are excellent when put to use by an expert who is adept in the manipulation of the many factors involved. The average Industrial Hygienist, by virtue of his widely diversified field of endeavor, is usually no such expert. He needs exposure values which express time-intensity relationships in terms of single numbers that will constitute benchmarks or guide lines. These benchmarks could then guide him in the estimation of the noise hazard.

Damage risk criteria presently accepted and in general use, are expressed in terms of 8 hours/day continuous exposure to a given noise spectrum.

In the Air Force and perhaps many other industries where noise presents a hazard, workers are seldom exposed to noise levels which exceed the damage risk criteria throughout the entire work day. Instead they are exposed to various high intensity noise spectra for brief intervals many times during the day. The problem of expressing this kind of exposure would be greatly simplified if the exposure could be equated in terms of an 8 hour continuous exposure for which fairly reliable data are available. WADC Tech Note 55-355[3] makes and supports the assumption that within certain maximum limits, equal quantities of acoustic energy will result in equal damage to hearing regardless of how the energy is distributed in time, provided the acoustic energy equals or exceeds damage risk criteria. On the basis of this concept, an equivalent noise exposure value may be calculated and utilized. For equal energy exposure, the ratio of sound energy at a higher noise level to the sound

[1] Industrial Hygiene Engineer, Surgeon's Office, Hq, San Antonio Air Materiel Area, Kelly AFB, Texas.

[2] 1st Lt, USAF, Sanitary & Industrial Hygiene Engineer, 7100th Hospital APO 633, New York, N. Y.

energy at a lower noise level is inversely proportional to the ratio of time of exposure at the higher noise level to the time of exposure at the lower noise level. Expressed mathematically, this relationship is:

E_1 = Energy at low noise level.
E_2 = Energy at high noise level.
T_1 = Time at low noise level.
T_2 = Time at high noise level.

$$(1) \quad \frac{E_2}{E_1} = \frac{T_1}{T_2}$$

Since most sound measuring instruments measure noise in units of decibels, the above relationship must be expressed in terms of decibels.

(2) db = 10 log E/E_R where E_R is the reference energy level.

Multiplying by 10, taking the log of each side and dividing the energy levels by E_R, equation (1) becomes:

$$(3) \quad 10 \log \frac{\frac{E_2}{E_R}}{\frac{E_1}{E_R}} = 10 \log \frac{T_1}{T_2}$$

or

$$(4) \quad 10 \log \frac{E_2}{E_R} - 10 \log \frac{E_1}{E_R} = 10 \log \frac{T_1}{T_2}$$

Substituting relationship (2)

$$(5) \quad db_2 - db_1 = 10 \log \frac{T_1}{T_2}$$

or

(6) $T_1 = T_2$ antilog 0.1 $(db_2 - db_1)$

In relationship (6), if db_1 is arbitrarily given a value of 85 and letting T_2 and db_2 be observed values, then T_1 will be the time of exposure at 85 db equivalent to exposure at the observed values. If we then define one equivalent exposure minute as a noise exposure equivalent to one minute at a sound pressure level of 85 db, T_1 will represent equivalent exposure time. Therefore, when expressed in terms of equivalent exposure time (EET), equation (6) becomes:

(7) EET = T antilog 0.1 (db − 85)

Where T and db are observed exposure time in minutes and sound pressure level in db Re .0002 dynes/CM^2 respectively.

A nomogram based on this equation can be easily constructed. Fig. 1 is a nomogram employed by the Air Force in AF Reg 160-3.[4]

Now that we have a common denominator for expressing exposure to different sound pressure levels for varying lengths of time, there remains only the task of establishing threshold limit values for the different kinds of noise spectra.

Since pain is usually considered a sign of damage to the body, the noise level in the ear canal should never be allowed to exceed the threshold for pain. Therefore, the unprotected ear should never be exposed to 135 db regardless of the length of the exposure time. Exposure to noise levels of 150 db and over often result in non auditory effects such as nausea, disorientation, vomiting, etc., even though the noise level in the ear canal is below 135 db. Consequently, personnel should never be exposed to 150 db and over for any length of time even though the ears are protected.

In the establishment of noise threshold limit values for the prevention of hearing loss, we are primarily concerned with protection of hearing in the speech communication frequency range. We are therefore concerned with the four octave bands between 300 and 4800 cps. Lifetime exposure limits can be expressed in terms of equivalent exposure time values for each of these four octave bands. These values should indicate when ear protection is recommended and when it is mandatory.

The ASA Z24-X-2 subcommittee report indicated that the lifetime hearing loss is minimal when the 8 hour daily exposure does not exceed 85 db of wide band noise. Converting an 85 db 8 hour exposure to equivalent exposure time, we find the value to be 480. We can therefore say that the use of ear protection is recommended for broad band noise when the EET value of 480 is exceeded in any octave band between 300 and 4800 cps.

Likewise, if we look at other accepted damage risk criteria we find that the damage risk curve for wide band noise falls along the 95 db line in the octave bands between 300 and 4800 cps.

A 95 db exposure for 8 hours is equal to an EET value of 4800. We may therefore state that the use of ear protection is mandatory for wide band noise when the EET value reaches 4800 in any of the four octave bands between 300 and 4800 cps.

Some noise will have pure tone components that concentrate the noise energy in one or more octave bands. While it is true that unprotected ears can tolerate exposure to noise levels higher than the lifetime limits when the exposure time is less than 8 hours, they cannot tolerate pure tone noise for as long an interval as broad band noise of the same level. The 8 hour continuous exposure damage risk criteria for pure tone and critical band noise is approximately 10 db less than the criteria for wide band noise. This means that the threshold limit for pure tone and criti-

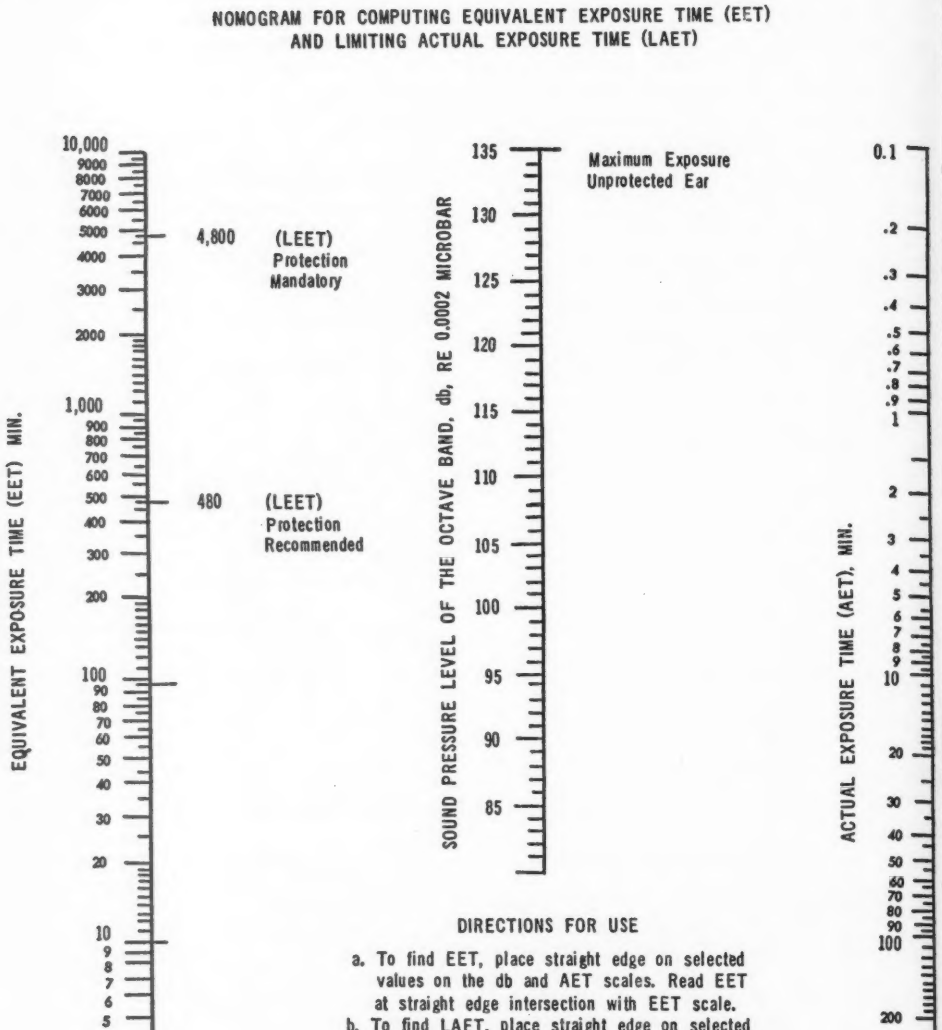

FIGURE 1

cal band noise must be less than that for wide band noise. It is not necessary, however, to develop a new set of threshold limit values for pure tone noise; instead, simply add 10 db to the measured SPL and treat the sound as wide band noise. Table I indicates the Limiting Equivalent Exposure Time (LEET) values which the Air Force uses as a guide.[4]

With threshold limits for unprotected ears established, a basis for determining the kind and amount of ear protection is also possible using the EET as a guide. Personnel exposed to noise may have their EET reduced in a number of ways. The individual's daily EET may be decreased by reducing the time spent in noise, the noise level in the ear canal, or both. For example, assume that a worker is exposed for 30 minutes a day to wide band noise with a SPL of 109 db in the 600–1200 cps octave band. Through the use of the nomogram (Fig. 1) it can be seen that the EET experienced by this individual has a value of 8000. This amount of exposure exceeds the threshold limit value of 4800 where ear protection is mandatory. By limiting the individual's exposure time to 15 minutes the EET is reduced to a value of 4000, which is below the value where ear protection is mandatory. Likewise, by reducing the exposure time to approximately two minutes no ear protection is recommended.

Reducing the exposure time to such short intervals is impractical. Again through the use of EET we may calculate the kind and/or the amount of ear protection needed so that the exposure time may be lengthened. The noise level in the ear canal may be lowered in several ways —by reducing the level of the noise field around the indvidual, by increasing the distance between the indivdual and the source, or by placing an acoustical barrier between the individual and the source. The ear protective acoustical barriers consist of devices which the individual wears to cover the external ear or to plug the external opening of the ear canal. These devices can be used singly or together, depending upon the amount of attenuation desired and the circumstances involved.

Table II taken from AFR 160-3[4] indicates the average amount of attenuation gained by these devices where an average fit is obtained. An example of how the EET values are used for evaluating the type of protection needed is as follows:

Take the 109 db noise previously referred to in the 600–1200 cps octave band. From Table II we see that a standard ear plug will reduce the noise level in the ear canal in this octave band by 18 db. Thus, we obtain an exposure noise level of 91 db. A 30 minute exposure to 91 db gives an EET value of 130. This value is lower than the threshold limit value of 480 so that we may then assume the individual is adequately protected by a standard ear plug.

On the other hand assume that an individual has a 30 minute exposure to a 130 db jet engine noise whose major component lies in the 600–1200 octave band. Again, if ear plugs are furnished the individual, the noise in the ear canal may be reduced by 18 db or to a level of 112 db. By consulting the nomogram we see that an exposure of 30 minutes to 112 db gives an EET value in excess of the threshold limit value of 4800. By adding an ear muff over the ear plug we get an attenuation of 28 db in the ear canal. Subtracting this from 130 db we obtain a noise level of 102 db in the ear canal. The EET for this noise level has a value which is below the threshold limit value of 4800.

And so it may be seen that in the use of EET values we have a very handy tool for noise evaluation and selection of proper ear protection.

A comparison of actual exposure in EET to the threshold limit values allows the Industrial Hygienist to evaluate the noise environment in much the same manner as other industrial hazards. As with other toxicology threshold limits, the threshold limit values for noise should be used as guides and not as absolute inflexible standards. They also do not apply to individuals with sensitive ears and in no way eliminate the requirements for audiometric examinations of exposed personnel. If future experience so indi-

TABLE I

Limiting Equivalent Exposure Times (LEET) for an 8-hour Day

Octave Band	LEET	Action Required
300–600 cps	480 minutes (8 hrs)	Use of ear protection is recommended when the EET for any band equals the value shown
600–1200 cps	480 minutes (8 hrs)	
1200–2400 cps	480 minutes (8 hrs)	
2400–4800 cps	480 minutes (8 hrs)	
300–600 cps	4800 minutes	Use of ear protection is mandatory when the EET for any band equals the value shown.
600–1200 cps	4800 minutes	
1200–2400 cps	4800 minutes	
2400–4800 cps	4800 minutes	

TABLE II

Average Octave Band Noise Level Reduction in Ear Canal Achieved by Use of Personal Protective Equiptment

Types of Equipment Used	BANDS			
	300–600 cps	600–1200 cps	1200–2400 cps	2400–4800–cps
Headset Earphone Covers	−7 db	−13 db	−20 db	−30 db
Standard Ear Plug or Ear Muff used alone	−14 db	−18 db	−25 db	−30 db
Standard Ear Plug and Ear Muff used together	−24 db	−28 db	−37 db	−40 db

cates, the numerical value of the threshold limits may be changed without requiring a change in the EET values. Though the EET values allow permissible limits to be defined in terms of single numbers, complete noise data are required. In order to calculate the noise exposure in EET, not only the noise intensity, in octave bands, but also the time duration of each intensity is required. To obtain these types of data the Industrial Hygienist is forced to make a thorough evaluation of the noise environment. These data, along with the threshold limit values, give him an excellent means for determining the possibility and the severity of a noise hazard.

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Critique

K. C. STEWART

University of Pittsburgh, Pittsburgh 13, Pa.

AS STATED, the basis of the noise exposure unit for providing hazard estimation is the equal energy concept; that is, $C_1 \times t_1 = C_2 \times t_2$.

Clearly, the hazard effect of noise is somehow related to noise energy (frequency distribution accounted for) and the time of application of this energy. A problem for hygienists is to come up with a means by which we can predict noise hazard, given some means of measuring energy, time relationships. Ideally, the total technique should provide hazard prediction for all types of noise exposures. This general case is probably beyond us at the moment, so we limit ourselves to consider first, steady noises which can be measured with present octave analyzer techniques, and then determine the time and motion pattern for men working in such steady noise. For the particular case at hand, I understand the technique to require octave measurements and time of exposure to the noise as measured. From these data, an amended exposure is calculated and related to an exposure which would be produced by a noise of the damage risk level operating for an eight hour day. If the total calculated equivalent exposure time per octave band falls below the limiting equivalent exposure time (based on present octave band criteria), then we say that the exposure is safe.

Before commenting further on the paper itself, and the possibilities of predicting hazardous noises offered by the technique, I should like to discuss some of the events that take place in the ear due to sound stimuli. These events may indicate some limitations to be expected in the present method. Consider, for example, the case of high intensity noise which lasts for only a fairly short time. We could specifically arrange matters so that the ear would not be traumatically damaged by this exposure, but would be damaged in a very short time. In this case, we have:

$$C_1 \times t_1 = \text{Hearing loss}$$

On the other hand, we could arrange to deliver the same energy over a relatively longer period of time so that no hearing loss would ensue. Now we have:

$$C_2 \times t_2 = \text{No hearing loss}$$

Yet,

$$C_1 \times t_1 = C_2 \times t_2$$

and an inconsistency in predicting hazard appears.

A second point to mention is the behavior of the ear to sound stimulus as the energy of stimulus increases. For simplicity, consider a single pure tone stimulus. At low levels of stimulation a small region of the basilar membrane is operative and the energy is concentrated there. As the stimulation energy increases, two events occur: (1) more cells are stimulated, that is, the region of excitation widens and (2) the amplitude of motion increases, so that the distribution of energy delivered to the cell changes from the previous instance. This only means that the attack on the hair cells is some complex function of energy level, since more hair cells

are brought into play as the intensity rises. A third factor to consider is the case of a very sharply rising noise function of extreme peak value occurring over a very small time interval, so that ear damping attenuates the ear response. The ear thus receives very little stimulation from: $C_3 \times t_3$, even though $C_3 \times t_3 = C_2 \times t_2 = C_1 \times t_1$. Again there appears to be an inconsistency relative to hazard prediction based on a linear $C \times t$ concept.

Another analogy can be drawn which sheds some light on the problem. Considering biologic response to ionizing radiation we have two different mechanisms of damage. One is genetic change and the other actual cell damage. For genetic change, it is felt that there is no MAC. However, for observable somatic change there is probably a limiting threshold level for which the cells are not damaged. Possibly below this level there are sub-microscopic changes, but, since we do not observe these changes we assume the change is reversible.

In the case of noise, we are probably dealing with the reversible case rather than the genetic. If this is so, there is some threshold of exposure, (however, exposure is defined) below which observed hearing damage does not occur, that is, the hair cells recover from the stimulus. This threshold is likely defined by complex exposure recovery functions. The implication we draw from a consideration of the above is that hearing loss is a function of concentration and time of exposure, but the function may not be simply concentration times time. The real need, of course, is to test the concept suggested in an experiment which compares, or validates, hearing loss and equivalent exposure time.

Some of the audience will recognize that the method outlined is closely allied with the noise dose concept as presented at some earlier meetings. There are one or two differences. Here the noise spectrum is described in octave bands in order to calculate an equivalent exposure time and the calculated values are related to a limiting equivalent exposure time based on present tentative damage risk criteria. This latter relation, of course, will simply be adjusted as future data requires.

On the other hand, our dose meter accounts for energy time functions, i.e. patterns, and also yields energy quanta which are based on certain meter weightings that are intended to account for some of the physiologic behavior of human hearing. Although the instrument takes spectrum into account, it does not do so in terms of octave bands. Also because of the specific instrument design, rapidly fluctuating noise is measurable. Our problem, nevertheless, and I believe that of the author also, will be to demonstrate that there is a workable relationship between equivalent exposure time and hearing loss caused by such exposure.

For both the EET and noise dose concepts, I feel that we require validating data before we generally accept the technique for hazard prediction. The same criticism can be leveled at present octave band techniques for these methods are not validated either. Furthermore, the present octave band analyzers are not usable in the measurement of a very large percentage of noise exposures. The real need of the hygienist, as stated at the beginning, is a method which employs an instrument and a technique in an overall experiment to define noise hazard. The challenge is considerable and we welcome new approaches such as Mr. Poth has given us.

Gordon Research Conferences

The Gordon Research Conferences for 1958 will be held from June 9 to August 29 at Colby Junior College, New London, New Hampshire; New Hampton School, New Hampton, New Hampshire and Kimball Union Academy, Meriden, New Hampshire.

The Conferences were established to stimulate research in universities, research foundations and industrial laboratories. This purpose is achieved by an informal type of meeting consisting of scheduled lectures and free discussion groups. Sufficient time is available to stimulate informal discussions among the members of a Conference. Meetings are held in the morning and in the evening, Monday through Friday, with the exception of Friday evening. The afternoons are available for participation in discussion groups as the individual desires. This type of meeting is a valuable means of disseminating information and ideas which otherwise would not be realized through the normal channels of publication and scientific meetings. In addition, scientists in related fields become acquainted and valuable associations are formed which result in collaboration and cooperative effort between different laboratories.

It is hoped that each Conference will extend the frontiers of science by fostering a free and informal exchange of ideas between persons actively interested in the subjects under discussion. The purpose of the program is not to review the known fields of chemistry but primarily to bring experts up to date as to the latest developments, analyze the significance of these developments, and to provoke suggestions as to underlying theories and profitable methods of approach for making new progress. In order to protect individual rights and to promote discussion, it is an established rule of each Conference that all information presented is not to be used without specific authorization of the individual making the contribution, whether in formal presentation or in discussion. No publications are prepared as emanating from the Conferences.

Individuals interested in attending a Conference are requested to send their applications to the Director. Each applicant must state the institution or company with which he is connected and the type of work in which he is most interested. Attendance at each Conference is limited to 100.

The complete program of the Conferences will be published in "Science" for February 28th. The Conference on Toxicology and Safety Evaluation will be held August 4–8 at Meriden, New Hampshire.

Requests for attendance at the Conferences, or for any additional information, should be addressed to W. George Parks, Director, Department of Chemistry, University of Rhode Island, Rhode Island. From June 9 to August 29, 1958 mail should be addressed to Colby Junior College, New London, New Hampshire.

The Toxicology of an Aniline-Furfuryl Alcohol-Hydrazine Vapor Mixture*

KEITH H. JACOBSON, WILLIAM E. RINEHART,† HENRY J. WHEELWRIGHT JR.,† MARTIN A. ROSS, LT COL, VC USA, JACKIE L. PAPIN, CAPT, CMLC, USA,† ROBERT C. DALY,† EARLE A. GREENE AND WILLIAM A. GROFF

Directorate of Medical Research, U. S. Army Chemical Warfare Laboratories, Army Chemical Center, Maryland

ANILINE, furfuryl alcohol, and hydrazine are important liquid propellants.[1] A mixture of the three containing 45% aniline, 45% furfuryl alcohol, and 7% hydrazine, with 3% water and other impurities, also has desirable propellant characteristics. In view of the toxic properties of the components, an investigation into the toxicology of the mixture has been carried out. This report describes the effects of single and repeated exposures of laboratory animals to vapors of this mixture.‡

The components have been characterized toxicologically in these Laboratories and elsewhere. Aniline is a toxic liquid, causing methemoglobinemia and its sequelae by various routes of administration.[4, 5, 6, 7] Furfuryl alcohol is a CNS depressant[8] and causes pulmonary damage.[4, 8] Hydrazine is a convulsant and respiratory irritant, as well as a hepatotoxin.[9, 10, 11] Comstock and Oberst[4] studied the toxicity of a vapor mixture consisting of 80% aniline and 20% furfuryl alcohol, and ascribed the toxic effects largely to the aniline component.

It seemed that the most likely source of vapors from this mixture would be from accidental spills of the liquid. Differential volatilization of the liquid components would produce a vapor with a different composition from the liquid. To simulate such volatilization, we used a method of dispersion whereby the liquid was dropped onto a surface continuously swept with air. Since the temperature of the surface would alter the composition of the vapor mixture, we arranged the dispersion apparatus to permit variation in the temperature of the dispersing surface.

Experimental Methods

A modification of the controlled dispersion apparatus described by Gray et al.[12] was used to achieve partial vaporization of the liquid mixture. This apparatus is shown in Figure 1. The mixture was dropped at a constant rate from a Mariotte bulb through a capillary onto a vertical gauze column where the mixture was partially vaporized by air passing through and over the gauze. The non-vaporized excess dripped into a vented reservoir. The vapors were drawn into a 0.7 cu. m. dynamic chamber. In the elevated temperature experiments, the mixture was volatilized at a temperature of 40–42°C (104–108°F) by passing the dispersing air over surface heated to this temperature. This was done by wrapping heating tape on the glass cylinder surrounding the dispersion surface. In the normal temperature experiments, the volatilization occurred at about 27°C. However, in both experiments the actual animal exposures took place at room temperature.

In studies of the toxicities of the individual components, vapors were dispersed by passing dry nitrogen through bubblers containing the liquid. Vapors were drawn into a 0.4 cu. m. dynamic chamber after being mixed with air in a pre-mixing bowl.

Chamber air samples were collected in glacial acetic acid. Aniline was determined colorimetrically after diazotization and coupling with N-naphthylethylenediamine dihydrochloride. Furfuryl alcohol was calculated by difference after determination of total bromine equivalence for the mixture. These methods are identical with those used by Comstock and Oberst;[4] a detailed description of the procedures appears in the Appendix at the end of this paper. Hydrazine was determined by a direct acidimetric titration[13] from another sample collected in 25% isopropanol, in acute exposures. In repeated exposures, where lower concentrations were present, determinations of hydrazine were made by an iodometric technique.[13]

* Presented at the Seventeenth Annual Meeting of the AIHA, Philadelphia, April 27, 1956.

† Present addresses: Mr. Rinehart, Department of Occupational Health, University of Pittsburgh, Pittsburgh, Pennsylvania. Dr. Wheelwright, 369 South Street, Pittsfield, Massachusetts.

Capt. Papin, 50th Cml Platoon, Fort Ord, California. Mr. Daly, Hudson Falls, R.D. 1, New York.

‡ The information in this report has previously been published in greater detail in two reports[2, 3] of limited availability.

Male rats from the Chemical Warfare Laboratories (CWL) colony (a derived Wistar strain), and female mice from the Biological Warfare Laboratories or CWL colonies (both derived CF1 strains) were used. In determinations of LC50's, 10 members of a species were exposed at each concentration level for a single 4 hour period. In repeated exposures, median survival times were computed from the deaths occurring in a group of 20 rats and 30 mice, compared with an equal number of controls. Additional rats, mice and in the case of repeated exposures, hamsters, were exposed for scheduled pathologic examination. Male beagle hounds, 3 to a group, with each group having a total weight of about 34 kg., were used in acute, subacute, and chronic exposures. Young cats, weighing from 1.4 to 1.8 kg. were used in acute exposures.

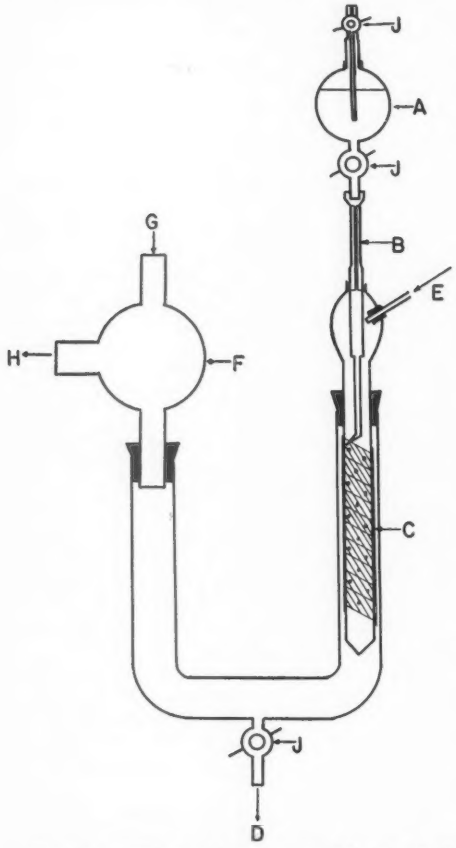

FIGURE 1.—The liquid mixture in Mariotte bulb (A) runs at constant rate through capillary (B) onto a gauze-wrapped perforated dispersing surface (C). Excess liquid drops into reservoir (D). Air under pressure enters at (E), passes through and over the dispersing surface and partially vaporizes the liquid mixture, and carries the vapors into a mixing bowl (F), where they are diluted by room air (G) and then drawn into the exposure chamber (H). In operation, stopcocks (J) are open. The overall height of the apparatus is approximately 36 inches.

LC50 values were computed by the Bliss-Finney method;[14] all deaths occurring during exposure and within 7 days thereafter were included in the computations. Median survival times in repeated exposures were computed from a time-response method of Bliss-Finney.[14]

Various clinical laboratory procedures were carried out on dogs, and in some instances on other species, to help characterize the toxic action of the vapor mixture. Red and white cell counts and hematocrit determinations were made by familiar methods.[15] Hemoglobin determinations were made by measuring the oxyhemoglobin of the blood, using the Klett-Summerson photoelectric colorimeter.[16] Sulfobromophthalein (BSP) retention was measured after intravenous injection of the dye (5 mg./kg.); a blood sample was withdrawn from another vein after 20 minutes. The serum was then alkalinized and the resulting color compared with a suitable standard in a photoelectric colorimeter.[17] A normal dog's liver clears 95% to 100% of the injected dye from the blood within 20 minutes. Bilirubin levels were determined by the method of Malloy and Evelyn, using photoelectric colorimetry.[18] Methemoglobin was determined by the method of Evelyn and Malloy[19] and was expressed in per cent as the ratio of methemoglobin to total hemoglobin. Non-protein nitrogen was measured by a micro-Kjeldahl method; the ammonia formed was determined colorimetrically after direct nesslerization of the digestion mixture.[16] Inorganic phosphorus in serum was determined by the method of Fiske and Subbarow[20] and the alkaline phosphatase was expressed as "Bodansky units" after incubation of a serum sample and comparison with a suitable standard.[21] The oxygen capacity of the blood was measured using venous blood withdrawn from a peripheral vein. The ability of this venous blood to become oxygenated was measured in the Van Slyke apparatus.[22] An artificial figure to represent the per cent of oxygen unsaturation to aid in the elucidation of the physiological mechanism was set up in the following relationship:

$$100 - \frac{100 \times \text{test oxygen capacity}}{\text{normal oxygen capacity}}$$

$$= \%\ O_2 \text{ unsaturation}$$

Thirteen volunteers participated in the 4 tests to determine the odor detectability of the mixture and of its components. Each subject sniffed various concentrations in an increasing geometric series of 2 until he detected an odor. The Fair-Wells osmoscope was used to effect the dilution of chamber atmospheres.[23] The subject's threshold level of odor detection was noted together with his description of the odor. The median detectable concentrations were calculated by the method of Bliss and Marks,[24] as modified by Finney.[14]

Experimental Results

Acute Exposures. In exposures of rodents to vapors dispersed at room temperature (*ca.* 27°C), the average composition of the vapor mixture was 5.9 volume % hydrazine, 46.9% aniline, and 47.2% furfuryl alcohol; at elevated temperature (*ca.* 40°C) dispersion, the mixture averaged 29.0% hydrazine, 47.2% aniline, and 23.8% furfuryl alcohol. Lethargy and cyanosis were seen in rats and mice at both dispersion temperatures. In addition, rats exposed to the vapor mixture dispersed at 40°C showed rapid and labored breathing; mice exposed to both types of mixtures developed tonicoclonic convulsions preceding death.

The logarithm of the concentration in total ppm of components plotted against the mortality probit resulted in a straight line relationship. Therefore, mortality data presented here are expressed in total ppm (the sum of the concentrations of the components) of the vapor mixture. LC50's for single 4 hour exposures at 27°C dispersion were 218 ppm for mice and 254 ppm for rats and at 40°C dispersion were 256 for mice and 298 for rats. The statistical information is summarized in Table I.

Dogs and cats exposed for 4 hours to vapor dispersed at room temperature developed cyanosis, tachypnea, vomiting, excessive salivation, and ataxia. One dog exposed at the highest concentration (215 ppm) had tonicoclonic convulsions after exposure. Cats were usually less active than dogs, and toxic signs in cats were less severe and less frequent than were those of dogs. Most dogs and cats were lethargic and dazed following acute exposures. Dogs lacked appetites for a day or two; in cats, this condition persisted for periods of several days to a week, and was probably a contributory cause of death in some instances. There were no significant changes in rectal temperatures or ECG's in dogs. Dogs were exposed to concentrations of from 153 total ppm, which killed no animals, to 215 ppm; one dog exposed to 215 ppm died overnight, while the other two were sacrificed in view of their severe intoxication believed likely to be followed by death. The mixture to which dogs were exposed averaged 17 volume % hydrazine, 49% aniline, and 34% furfuryl alcohol; in exposures of cats, the mixture averaged 30% hydrazine, 45% aniline, and 25% furfuryl alcohol. Cats were exposed to concentrations of from 128 to 160 ppm; 2 of 3 exposed cats died at the highest concentration and 3 of 3 at the lowest, where failure to eat was most pronounced.

TABLE I

LC50 Values for Rodents Exposed 4 Hours

Agent	Species	LC50 (ppm) and 19/20 Confidence Limits	Slope	S.E. of Slope
Aniline-Furfuryl Alcohol-Hydrazine (Dispersed at 27°C)	Rats	254 (244-282)	22.1	7.6
	Mice	218 (211-225)	23.5	4.3
Aniline-Furfuryl Alcohol-Hydrazine (Dispersed at 40°C)	Rats	298 (292-309)	49.9	15.4
	Mice	256 (249-265)	42.2	10.6
Furfuryl Alcohol	Rats	233 (226-240)	14.0	1.8
Hydrazine	Rats	570 (504-649)*	7.3	1.8
	Mice	252 (? -305)*	3.8	1.6
Aniline	Rats	Approx. 600†	—	—

* from reference 10.

† inferred from data in reference 4.

To compare the toxicity of the mixture with the toxicities of the components, rats were exposed to each component. Four hour exposure of 10 rats to 605 ppm of hydrazine caused 6 deaths, which seems consistent with an LC50 value of 570 ppm.[10] Similar exposure of 10 rats to aniline vapor at 520 ppm caused 2 deaths, which seems consistent with an LC50 value of 600 ppm inferred from data of Comstock and Oberst.[4] Preliminary tests with furfury alcohol indicated that it was more toxic than had been suggested by previous work,[4] so the concentration-mortality curve was determined. The LC50 for rats computed from this curve was 233 ppm for 4 hour exposure. Other statistics are shown in Table I.

In all dogs, cats, and rats, the amount of methemoglobin was increased over control values immediately after removal from the gassing

TABLE II
Vapor Concentrations in Repeated Exposures

Test	Species	No. of Exposures*	Total Vapor Mixture		Concentration of Constituents		
			Mean Concentration	S.D.	Aniline	Furfuryl Alcohol	Hydrazine
			ppm	ppm	ppm	ppm	ppm
Subacute (6 Weeks)	Rats	27	90	6	44.1	40.9	5.0
	Mice	22	89	6	44.3	39.8	4.9
	Hamsters	29	91	6	44.1	41.8	5.1
	Dogs	30	51	5	23.0	23.0	5.0
Chronic (5-8 Months)	Rats	162	13.8	1.3	7.7	4.6	1.5
	Mice	162	13.8	1.3	7.7	4.6	1.5
	Hamsters	109	13.9	1.5	7.6	4.5	1.8
	Dogs	124	14.5	1.4	6.4	5.2	2.9

* Each exposure period was 6 hours; exposures were conducted 5 days per week.

chamber. Rat blood contained from 20 to 30% methemoglobin at both normal and elevated dispersion temperature experiments. These results could not be correlated with the amount of aniline vapor present in any exposure. In dogs, methemoglobin rise was reflected by a fall in the oxygen capacity of the peripheral venous blood, and likewise by the rise in the percentage of oxygen unsaturation, which characterized the defect in more physiological terms. These effects occurred rapidly; however, in most instances the values in survivors returned to normal or near normal at the end of 24 hours. The extent of the alteration of these values paralleled the change in concentration of the vapor mixture.

Serum bilirubin values did not change significantly in dogs exposed to the lower concentrations. In one animal that was exposed to a higher concentration, and which survived more than 24 hours, a rise in total bilirubin occurred when the animal was near death. The rise was contributed chiefly by the indirect fraction. NPN levels remained within normal limits except for a dog near death; this change in NPN was presumed to be due to renal ischemia. BSP retention was measured in 5 dogs, and in 2 of these, values were recorded only for the period of one hour after gassing; in the other 3, the test was also performed one day later. All results were within normal limits.

RBC, WBC, hemoglobin, and hematocrit were not significantly altered in exposed dogs, except for an occasional mild elevation of RBC, hemoglobin, and hematocrit; this probably represents hemoconcentration secondary to dehydration. One moribund animal showed leucocytosis.

Post-mortem examination of rats and mice revealed pulmonary edema in about half the animals, combined with minor degrees of pulmonary hemorrhage probably due to hypoxia. Examination of cats similarly exposed revealed in some instances pulmonary edema and subpleural hemorrhages, mild tubular degeneration of the kidneys, fatty metamorphosis of the liver in the central zones, and marked anoxic cell changes in the cerebral cortex. Three of the dogs that were autopsied showed similar anoxic changes characterized by some renal tubular degeneration and marked ischemic degeneration of the ganglion cells of the brain. In one animal there was fatty metamorphosis in the central area of the liver lobule. There were no pulmonary lesions in dogs attributable to exposure.

Subacute Exposures. Subacute exposures involved daily 6 hour exposures for 5 days a week for 6 weeks. Rats and mice so exposed to 90 ppm* developed cyanosis, tachypnea, lethargy, and weight loss. All rats and mice died during the 6 weeks period. There were no experimental deaths in hamsters exposed to 90 ppm; the only sign noted was weight loss. The median survival times for both rats and mice was 16 exposures with 95% confidence limits of 15 to 17 days. No control animals died.

Dogs exposed to 51 ppm showed cyanosis, tachypnea, lethargy, loss of weight, a transient loss of appetite, and occasional vomiting. Hematologic studies showed falls in RBC, hemoglobin, and hematocrit by the end of the second week, with a return to nearly normal levels by the end of the 6 week period. There was an increase in both direct and indirect serum bilirubin at the end of the first week in 2 of 3 dogs, with a steady decline toward initial values by the end

* Mean concentrations, standard deviations, and compositions for subacute and chronic exposures are shown in Table II.

of the sixth week. Two dogs showed a transient increase in BSP retention. There was a significant elevation of alkaline phosphatase in all dogs during the second week, declining to control or near control levels in 2 of the dogs by the sixth week. Conversion of hemoglobin to methemoglobin, with a concomitant fall in oxygen capacity to about one-half normal values, occurred during the first 2 weeks. Methemoglobin/hemoglobin ratios declined to normal by the last 2 weeks of the period. A slight but definite increase in blood NPN was seen by the sixth week. Tables showing the results of hematological and blood chemistry studies appear in the Appendix.

Microscopic examination of all viscera of dogs showed only changes attributable to hemolysis and hypoxia. The liver showed centrilobular degeneration and congestion; the lungs showed occasional petechiae. In rodents, the changes were confined to the spleen, in which marked hemosiderosis and extra-medullary hematopoiesis were seen.

Chronic Exposures. Chronic exposures were carried out at a level of about 14 ppm for 6 hours a day, 5 days a week, for about 5 months for hamsters, 6 months for dogs, and 8 months for rats and mice. There were no toxic signs other than a lesser weight gain in exposed rodents than in controls.

Dogs showed no effects attributable to exposure. Hematologic and clinical chemistry values were within normal limits. Examination of tissues did not reveal changes which could be unequivocally attributed to exposure; the slight hemosiderosis noted in the spleen and liver was no more prominent than that seen in normal dogs.

Tissues from rodents sacrificed at intervals during exposure showed a possibly significant increase in hemosiderin deposition and extramedullary hematopoiesis in the spleen.

Hazard Index. In an attempt to get information on the vapor hazard of the liquid mixture, e.g. as a "hazard index",[25] which is the ratio of saturation concentration to LC50, we used the dispersion apparatus described previously to measure volatility. When liquid flow, vaporization and chamber air flow are kept constant, the concentration found in the chamber should be proportional to the volatility of the fuel mixture, and therefore to the saturation concentration, when concentrations are expressed in ppm*. The proportionality constant was determined from the known vapor pressures of the components[13, 26] and the concentrations found in the chamber after dispersion from the described apparatus under constant flow conditions. This ratio was about the same for aniline and furfuryl alcohol, but the ratio for hydrazine was appreciably different, and in the direction that would be anticipated from the known sorptive characteristics of hydrazine.[9, 10] Using these calculated saturations concentrations and LC50 values (at 27°C dispersion) shown in Table I, we estimated indices of about 2 for the mixture, for rats and mice. Thus, the mixture has a vapor hazard index similar to that of aniline, which has a value of about 1 for rats, and furfuryl alcohol, which has a value of about 3 for rats; also, the mixture has an appreciably lower hazard index than hydrazine, which has indices of 33 for rats and 75 for mice.[10] The indices for the mixture are partially in error because the total concentration of the mixture found in the chamber was less than would be expected from the amount dispersed, due to the sorption of hydrazine; we do not believe this error has more than theoretical implications.

Odor Detection. The vapor mixture used for sniff tests contained 9% hydrazine, 46% aniline, and 45% furfuryl alcohol. Human subjects sniffing the vapor mixture and the component vapors could generally detect all vapors at values around 10 ppm. The median detectable concentrations are shown in Table III. The same 13 subjects took part in all tests. Hydrazine was most generally described as "irritating", "sweet", and "pungent". Furfuryl alcohol was described as "sweet", "alcoholic", and "ether-like". Aniline was described as "sweet", or "aromatic" as well as several descriptions of "like rubber". The mixture was mostly frequently described as "sweet", "aromatic", or "rubber-like"; most subjects described the mixture as smelling more like aniline than the other components. It was shown by statistical methods[14, 24] that the detection of the mixture by odor was an additive effect of the proportions of the components and their respective potencies when a common slope of the response curve is assumed. Hydrazine has been previously described[10] as ammoniacal or amine-like. We have no explanation as to why a similar description was not elicited in this case. Some of the same volunteers who participated in the previous test also took part in this test, and affirmed that the hydrazine did not have the same odor as before. It is interesting to note that the median concentration of hydrazine detectable by odor described in Table III is about the same as that previously reported.[10]

* The concentration found in the chamber also depends on latent heat of vaporization. In view of other errors involved in estimation of hazard indices and the undesirability of precise application of such indices in industrial hygiene practice, this variable has not been considered.

TABLE III

Odor Detection of Aniline, Furfuryl Alcohol Hydrazine, and Their Mixture

Agent	Median Detectable Concentration	19/20 Confidence Limits	Slope	Median Detectable Concentrations Assuming Slope of 2.4
	ppm	*ppm*		*ppm*
Mixture	7	4–10	2.7	6
Hydrazine	4	3–7	3.2	4
Furfuryl Alcohol	8	4–17	1.9	7
Aniline	10	6–16	2.3	10

Comment

Variations in composition of the vapor mixture reported in the various exposures described are believed to be due to variations in sorption of the vapors as a result of varying amounts, and perhaps types, of surfaces encountered with different animal species, as well as the effect of excreta. These surface effects would be expected to affect mainly the hydrazine concentrations, with resulting variations in proportions of other components. While our experimental dispersing surface does not duplicate surfaces used operationally, we believe the data obtained have some application, since vaporization from surfaces will vary for several reasons, one of which is temperature variation, and will result in vapor mixtures of various compositions. Under conditions favoring an increased proportion of the most toxic component, furfuryl alcohol, (as at 27°C dispersion), the mixture would be expected to be slightly more toxic than under conditions yielding lower proportions of furfuryl alcohol (as at 40°C dispersion).

Evaluation of the data obtained from laboratory studies on the blood of dogs, cats, and rats, combined with studies of tissue changes, permits some conclusions to be made on the abnormalities caused by exposures to vapors of this mixture. Within one hour after removal from acute exposures, the methemoglobin content increased, producing: (1) a rise in the methemoglobin/hemoglobin ratio, (2) a depression of the oxygen-carrying capacity of the blood, and (3) an increase in oxygen unsaturation. It would appear that if dogs' hemoglobin were oxygenated to not more than 50% of its total capacity, i.e. if methemoglobin replaced oxyhemoglobin to that extent, survival was unlikely. However, since the values returned to normal or near normal at the end of 24 hours in surviving animals, it would appear that the natural homeostatic mechanisms were quite active and efficient. In dogs that had severe enough oxygen unsaturation, some other chemical changes in the blood occurred, which were secondary to anoxemia. One animal that was near death showed a rise in bilirubin and a high NPN value, presumably from renal ischemia. The significance of these changes is obscure because of the many factors operating in any terminal condition, but it could have been due to the anoxemic changes brought on by the aniline poisoning. The consistent normality of BSP excretion would indicate that the liver was not affected in this period of time. Post-mortem examinations of the several species revealed changes secondary to the prevalent hypoxemia involving the brain, kidneys, and liver, and lungs.

Repeated exposures of dogs and rodents to vapor concentrations of 50 to 90 ppm for 6 weeks caused production of methemoglobin, with a consequent decrease in oxygen capacity of the blood, acute hemolytic anemia, and hypoxemia. Histologic changes were evident as varying degrees of centrilobular atrophy and congestion of the liver as well as extra-medullary hematopoiesis and hemosiderosis in the spleen. Six to eight months exposure to vapor levels of 14 ppm produced no significant toxic effects.

In single exposures, the toxicity of the mixture, based on LC50 values in Table I, was greater than would be predicted from the proportion and potency of each component vapor. Statistical analysis shows that the mixture is about 30% more toxic than would be expected if the effects were additive. We found no reason to believe potentiation of toxicity occurred on repeated exposures. However, more information on the effects of chronic exposure to furfuryl alcohol would be needed before potentiation could be adequately shown. If furfuryl alcohol were found to have an MAC of 5 ppm (which we believe to be near the proper value), it would appear that no potentiation occurred. Thus, available evidence suggests that the safe vapor concentration of this mixture, at least in proportions similar to those used in these experiments, may be described by the MAC's of the components.

Summary

Single or repeated exposure of laboratory animals to vapors dispersed from a liquid mixture composed of 45% aniline, 45% furfuryl alcohol, and 7% hydrazine caused the formation of methemoglobin with a resulting decrease in

oxygen capacity of the blood and anoxemic tissue changes. Some hemolysis was noted on repeated exposures.

The acute toxicity of the mixture was slightly greater than would be expected from the proportions and potencies of the components present in the mixture. While the possibility of potentiation of toxicity on chronic exposures cannot be fully evaluated until more information on the chronic toxicity of furfuryl alcohol is obtained, it does not appear probable that significant potentiation occurred on repeated exposure. Thus, if the safe levels of the components are not exceeded, exposure to a mixture of these components should also be safe.

Human subjects smelling the vapor through an osmoscope could generally detect the mixture, as well as the components, at levels of about 10 ppm. The mixture was described as smelling more like aniline than like any of the other components.

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Appendix

Analysis of an Aniline-Furfuryl Alcohol-Hydrazine Mixture

Two samples were drawn simultaneously, if possible. Otherwise, they were drawn as close together in time as was expedient to avoid error from chamber concentration fluctuations. Forty ml. of 25% isopropanol were placed in one Edge-

wood bubbler. An air sample was drawn at a rate not greater than 1.5 liters/min. When a sufficient sample had been drawn to contain 8–12 mg. of hydrazine, the bubbler contents were transferred into an Erlenmeyer flask, and the bubbler was washed with more of the 25% isopropanol used for collection. The hydrazine was determined acidimetrically.

Thirty to 40 ml. of glacial acetic acid were placed in a second Edgewood bubbler. Collection methods were the same as above. Sample size was determined by expected concentration. The contents of the bubbler were transferred, by washing the bubbler with glacial acetic acid, into a 100 ml. volumetric flask and made to volume with glacial acetic acid. After thorough mixing, a 5 ml. aliquot was transferred to a 25 ml. volumetric flask and diluted to the mark with distilled water. One ml. portions were used for the analysis by a colorimetric diazotization method for aniline. These 1 ml. portions contained from 15–40 micrograms aniline/ml. Other aliquots from the original glacial acetic acid sample were brominated to give a total bromine equivalent. Furfuryl alcohol was determined by difference from the total for the known values of hydrazine and aniline as calculated from the specific determinations of these components.

ANALYSIS AND CALCULATION (Note 1)

1. Hydrazine.

The collected sample was titrated in 25% isopropanol with standard 0.5 N HCl to a methylene blue-methyl red endpoint. (Note 2).

$$\frac{\text{mg.} \times \text{N} \times 32.05}{\text{volume of sample}} = \text{mg./l.}$$

$$\text{mg./l.} \times 764 = \text{ppm}$$

$$\text{mg./l.} \times 0.1248 = \text{meq. } Br_2\text{/l.}$$

2. Aniline. (Note 3)

A 1 ml. aliquot of the acetic acid-water dilution was placed in a 25 ml. volumetric flask. Four ml. of water and 0.5 ml. of 0.2% sodium nitrite were added. This was allowed to stand for 10 min. Then 0.5 ml. of 1% ammonium sulfamate was added. This was allowed to stand for 3 min. One ml. 30% sodium acetate and 0.5 ml. of 0.2% N-(1-naphthyl)-ethylenediamine dihydrochloride were added. This was allowed to stand 20 min. for color development. Then 0.5 ml. conc. HCl was added. This was diluted to volume with water. The sample was read on a Klett-Summerson colorimeter using a #54 (green) filter. A reagent blank was run using 20% acetic acid in place of the sample. Results were compared with a calibrated curve for aniline.

$$\frac{\text{micrograms aniline} \times \text{dilution}}{1000 \times \text{volume of sample}} = \text{mg./l.}$$

$$\text{mg./l.} \times 263 = \text{ppm}$$

$$\text{mg./l.} \times 0.0645 = \text{meq. } Br_2\text{/l.}$$

3. Furfuryl Alcohol. (Notes 4 and 5)

Aliquots of the original glacial acetic acid sample were placed in Wijs iodine flasks and a measured known excess of 0.06–0.07 N pyridine-bromine-sulfate solution was added. These were stoppered and sealed with 10% potassium iodide solution. This was allowed to stand in the dark for 1 hr. Sufficient 10% potassium iodide was added to insure complete liberation of iodine from the excess bromine and titration was done with standard 0.06–0.07 N sodium thiosulfate to a starch-indicator endpoint.

$$\frac{(\text{ml.}_{\text{PBS}} \times \text{N} - \text{ml.}_{\text{thio}} \times \text{N}) \times \text{dilution}}{\text{volume of sample}} = \text{total meq. } Br_2\text{/l.}$$

Total meq. Br_2/l. — sum of Br_2 meq./l. (aniline and hydrazine) =

meq. Br_2/l. for furfuryl alcohol

Net meq. Br_2/l. $\times$ 24.5 = mg./l.

mg./l. $\times$ 249.5 = ppm

NOTES

1. To assay the liquid mixture, samples were weighed directly, dilutions were made, and analysis was done by the methods described for the vapors.

2. Experience in this Laboratory has shown that 0.5 N acid must be used to obtain a good endpoint. Since this results in a rather small titer, it is suggested that a microburet be used. The endpoint occurred at a slightly acid pH; therefore an indicator turning color at a pH of 4–5 is suggested.

3. Times given are minimum safe times for complete reaction to take place.

4. Preparation of Pyridine-Bromine-Sulfate (PBS) reagent: Forty ml. glacial acetic acid were placed in each of 3 dry Erlenmeyer flasks. Sixteen ml. pyridine were added to the first. Eleven ml. concentrated sulfuric acid were added to the second. When cool, these were combined and again cooled. Five ml. pure liquid bromine were added to the third. This was added to the previous mixture and diluted to two liters with glacial acetic acid. It was mixed by shaking.

5. PBS was carefully restandardized every few days, or daily blank determinations were made.

TABLE IV

Hematological Values of Dogs After Subacute Exposures to Aniline-Furfuryl Alcohol-Hydrazine Vapor Mixture

Week of Exposure	Experimental Dog No.											
	369				353				367			
	Red Blood Cells	Hemoglobin	Hematocrit	Reticulocytes	Red Blood Cells	Hemoglobin	Hematocrit	Reticulocytes	Red Blood Cells	Hemoglobin	Hematocrit	Reticulocytes
	10^6/mm.^{3} of blood	g./100 cc	%	%	10^6/mm.^{3} of blood	g./100 cc	%	%	10^6/mm.^{3} of blood	g./100 cc.	%	%
Preexposure	7.0	12.9	45.0	0.2	7.6	13.7	44.0	0.3	6.8	14.1	44.0	0.2
1	7.8	14.9	42.4	0.1	8.7	18.3	54.0	0.2	6.7	13.9	38.0	0.2
2	3.3	8.9	25.5	0.6	4.6	10.4	30.0	0.5	4.3	7.1	17.5	1.1
3	5.3	10.4	31.5	2.1	5.1	10.3	22.0	0.8	3.7	6.7	12.5	0.6
4	5.8	9.4	32.0	0.6	6.0	10.2	33.0	0.4	4.0	9.2	28.5	1.3
5	7.3	—	38.5	0.2	5.6	10.4	33.0	0.3	6.0	9.8	31.0	0.5
6	6.9	10.5	34.5	0.2	6.5	11.6	38.0	0.3	5.5	8.8	32.0	0.4
	Control Dog No.											
	E-1				65				182			
Preexposure	8.7	15.7	52.5	0.4	6.11	11.9	35.5	0.2	8.3	16.2	48.0	0.3
1	8.1	15.6	48.0	0.3	6.0	12.2	36.0	0.3	7.9	16.4	47.5	0.1
2	8.0	16.6	48.5	0.2	7.0	12.8	38.0	0.4	7.9	16.5	48.0	0.3
3	5.8	16.8	46.0	0.4	5.3	11.0	31.5	0.3	6.1	16.8	45.0	0.2
4	—	16.2	44.0	—	—	11.0	32.0	—	—	16.3	45.0	—
5	—	15.8	49.0	—	—	11.4	38.0	—	—	15.8	47.5	—
6	—	15.9	46.5	—	—	10.9	32.5	—	—	15.9	50.5	—

TABLE V

Determination of Bilirubin in Blood of Dogs After Subacute Exposure to Aniline-Furfuryl Alcohol-Hydrazine Vapor Mixture

Week of Exposure	Total Bilirubin			Direct Bilirubin			Indirect Bilirubin		
	Experimental Dog No.			Experimental Dog No.			Experimental Dog No.		
	369	353	367	369	353	367	369	353	367
	mg./100 ml. of serum								
Preexposure	0.0	0.0	0.048	0.0	0.0	0.024	0.0	0.0	0.024
1	6.4	5.9	0.63	3.9	3.7	0.22	2.5	2.2	0.41
2	0.78	2.8	0.39	0.39	1.3	0.17	0.39	1.5	0.22
3	0.54	1.3	0.25	0.27	0.6	0.10	0.27	0.7	0.15
4	0.29	0.92	0.19	0.15	0.49	0.07	0.14	0.43	0.12
5	0.83	1.02	0.24	0.39	0.44	0.07	0.44	0.58	0.17
6	—	—	—	—	—	—	—	—	—
	Control Dog No.			Control Dog No.			Control Dog No.		
	E-1	65	182	E-1	65	182	E-1	65	182
Preexposure	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	0.048	0.0	0.0	0.024	0.0	0.0	0.024	0.0	0.0
3	0.024	0.0	0.0	0.0	0.0	0.0	0.024	0.0	0.0
4	—	—	—	—	—	—	—	—	—
5	—	—	—	—	—	—	—	—	—
6	—	—	—	—	—	—	—	—	—

Normal total bilirubin values for beagle dogs at these Laboratories are 0–0.2 mg./100 ml. serum.

TABLE VI

Values From Several Liver Function Tests on Dogs After Subacute Exposures to Aniline-Furfuryl Alcohol-Hydrazine Vapor Mixture

Week of Exposure	BSP Retention After 20 Min.			Inorganic Phosphorus			Alkaline Phosphatase		
	Experimental Dog No.			Experimental Dog No.			Experimental Dog No.		
	369	353	367	369	353	367	369	353	367
		%		mg./100 ml.			Bodansky Units		
Preexposure	—	—	—	—	—	—	—	—	—
1	—	—	—	—	—	—	—	—	—
2	24.5	45.1	8.4	3.9	4.1	4.4	5.4	15.1	4.7
3	8.2	11.8	—	5.9	5.1	5.6	4.8	10.8	3.6
4	4.3	10.6	1.7	5.6	4.9	4.8	3.8	3.6	6.7
5	20.9	12.2	3.4	4.0	4.3	7.3	11.9	5.3	3.1
6	5.3	6.5	6.3	4.1	4.6	5.2	5.4	4.6	3.0
	Control Dog No.			Control Dog No.			Control Dog No.		
	E-1	65	182	E-1	65	182	E-1	65	182
Preexposure	—	—	—	—	—	—	—	—	—
1	—	—	—	—	—	—	—	—	—
2	—	—	—	—	—	—	—	—	—
3	—	—	—	—	—	—	—	—	—
4	3.4	2.6	4.6	3.2	4.4	3.4	1.5	2.5	1.6
5	—	—	—	—	—	—	—	—	—
6	—	—	—	—	—	—	—	—	—

Normal BSP retention for beagle dogs at these Laboratories is in the range of 0–5% (in plasma); normal inorganic phosphorus values are 2.5–5.5 mg./100 ml. serum; normal alkaline phosphatase values are 1.5–3.5 units (in serum).

TABLE VII

Oxygen Combining Capacity and Amount of Methemoglobin in Blood of Dogs After Subacute Exposures to Aniline-Furfuryl Alcohol-Hydrazine Vapor Mixture

Week of Exposure	O_2 Capacity						Methemoglobin/hemoglobin					
	Experimental Dog No.			Control Dog No.			Experimental Dog No.			Control Dog No.		
	369	353	367	E-1	65	182	369	353	367	E-1	65	182
	vol. %						%					
Preexposure	19.7	21.1	20.7	20.4	16.9	23.6	0.4	0.5	1.4	0.8	1.1	0.0
1	19.9	25.4	18.5	21.2	16.0	22.7	2.6	0.9	1.9	1.4	1.1	1.4
2	11.9	13.8	8.7	26.0	17.2	24.8	5.5	2.8	3.9	0.3	0.0	0.3
3	14.3	13.8	9.1	23.2	16.1	23.6	1.5	1.5	3.5	0.6	2.4	0.9
4	—	—	—	—	—	—	1.6	7.2	5.7	0.2	0.0	0.2
5	—	—	—	—	—	—	0.6	0.7	1.0	0.3	0.0	0.7
6	—	—	—	—	—	—	0.3	1.2	0.3	0.5	0.2	1.0

Normal O_2 capacity for beagle dogs at these Laboratories ranges from 18–26 vol. %; normal methemoglobin-hemoglobin ratios are 0–2%.

TABLE VIII

Nonprotein Nitrogen (NPN) Determinations on Blood of Dogs After Subacute Exposures to Aniline-Furfuryl Alcohol-Hydrazine Vapor Mixture

Week of Exposure	NPN					
	Experimental Dog No.			Control Dog No.		
	369	353	367	E-1	65	182
	mg. %					
Preexposure	27.6	28.5	26.7	27.6	28.5	27.1
1	39.6	37.7	41.2	30.8	33.4	38.8
2	34.2	32.6	25.4	32.1	26.8	29.4
3	30.8	29.9	19.4	27.2	25.7	29.4
4	24.8	41.3	24.8	26.0	23.3	25.7
5	44.9	44.9	39.9	24.4	22.1	30.3
6	62.4	61.1	65.0	37.9	39.7	30.8

Normal NPN range for beagle dogs at these Laboratories is 17–40 mg./100 ml. blood.

Nuclear Safety and Industrial Hygiene in the Fabrication of Nuclear Fuel Elements

W. B. HARRIS AND L. R. SOLON

Health and Safety Laboratory, New York Operations Office, U. S. Atomic Energy Commission

Industrial experience with the production of enriched fuel elements is reviewed briefly. Essential factors for the prevention of criticality incidents are outlined and discussed, and general criteria are given for the insurance of nuclear safety and health protection. Descriptions of specific processes and processing equipment are included, as are airborne concentrations which might be expected to result from the use of this equipment.

THE BASIC fuel of the nuclear reactor, whether the reactor be for research or for power production, is the isotope of uranium with an atomic weight of 235. Though one can operate a reactor on a fuel containing the normal isotopic content of uranium 235, which is 7/10 of 1%, the neutron economy of any reactor increases in general with an increase in the U-235 proportion. Most reactors which have been designed recently contain fuels with some degree of U-235 enrichment. The low enrichment reactors usually have fuels containing between 1.2%, and 5 or 6% of U-235. Other reactors will contain a fuel having a U-235 enrichment to about 20–25%, while those reactors requiring extremely high neutron fluxes will contain fuel which is enriched to about 90% in U-235.

Because of the high chemical reactivity of uranium and because of certain thermal instabilities, the fuel elements which go into the reactor are usually covered with some type of cladding material. The cladding materials which have been used generally to date have been aluminum, which is used under most normal circumstances, and zirconium where the corrosion specifications are especially severe. Other types of cladding materials, especially plastics, have been used in certain low power reactors. The dilution of the U-235 may either be in normal uranium or in some other type of matrix. Those materials which have been used are thorium, aluminum, and zirconium, although others can be successfully employed.

In the fabrication of fuel elements there are three basic differences between the use of normal uranium and uranium which is enriched in U-235. In the first instance, because of its cost and its application, very rigid controls have been set up requiring accounting for minute amounts of U-235. This presupposes retention of such things as wiping cloths and papers; broken bottles, and pieces of metal which have come in contact with the material; exhaust system filters, and other similar components which may have become contaminated. These are saved, and the material is recovered from them.

A second major area of difference involves an increase in the specific alpha activity which one finds as the uranium is enriched in the U-235 isotope. Although the specific activity of U-235 is only greater than that of U-238 by a factor of 15, the presence of the very small mass of U-234 isotope in the original mixture governs the overall specific activity of the final enriched substance since the U-234 content is increased at the same time as the U-235. In Fig. 1 can be seen the manner in which the maximum permissible weight concentration changes with enrichment. (This presumes that the permissible radioactivity is the same for all values of enrichment.) As can be seen from the curve, the same degree of radioactivity as comes from a given quantity of normal uranium is contributed by about 1% of that quantity of fully enriched material. Since the maximum allowable weight concentration of natural uranium in the air is about 1/10 of a milligram/cubic meter, the permissible concentration of fully enriched uranium is of the order of 1 ug/M^3.

A third and probably the most important difference between enriched materials and normal materials is that of criticality. Before discussing the limitations which are placed on a handling procedure by the factors of criticality, it might be well to review briefly the physical phenomenon which imposes these restrictions.

The U-235 nucleus consists of 92 protons, and 235 minus 92, or 143 neutrons. When an additional neutron enters the U-235 nucleus, a new nucleus is formed in a configuration of great in-

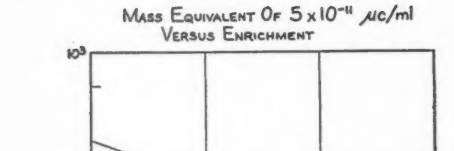


FIGURE 1

stability. This resulting nucleus, in seeking a more stable configuration splits into two new nuclei of approximately equal size, leaving over a surplus of 2 or 3 additional neutrons. If additional U-235 atoms are present in a suitable distribution, one of these surplus neutrons can be captured by a neighboring nucleus which in turn will experience similar fission. If sufficient neutron economy can be achieved, the result is the fission chain reaction, and the resulting assembly is called critical. The capture of a neutron by a U-235 atom is facilitated with neutrons of very low energy so that those elements of low atomic weight, such as hydrogen, beryllium, and carbon, which reduce neutron energy by essentially billiard ball collisions, will tend to improve the chances of fission. These are called moderators.

It is the function of the reactor designer to effect neutron economy in such a way that conditions for the chain reaction are most readily realized. On the other hand, it is the purpose of the person responsible for nuclear safety in handling fissionable materials to see that the chain reaction is not realized during storage or fabrication. Nuclear safety is achieved in general by limiting the mass or concentration in a particular location or by designing processing apparatus, shipping containers, and storage facilities so that the geometry for fission is always unfavorable.

In order to achieve health protection, safety and economy in the handling of enriched uranium materials there are several basic criteria which must be recognized:

1. The uranium must be handled in such a way that a minimum amount of oxidation occurs. This will tend to reduce airborne concentrations.

2. Where there is a possibility of some oxidation or vaporization of the material, the operation should be carried out with suitable ventilation or in a complete enclosure.

3. Operations involving highly alloyed materials are generally much safer than those which use high concentrations of uranium.

4. Any material which has been heated to a high temperature is a potential contaminating material.

5. Any rough handling, such as punching, hammering, and so forth, will tend to give rise to airborne concentrations.

6. Handling of uranium powders is obviously the most dangerous procedure from the health standpoint and should be provided with the most careful controls.

7. Extreme effort should be made to insure no loss of material. This means careful filtration of air effluents, strict containment of the material, and wiping up of any area wherever contamination may exist.

8. Care should be exercised not to mix materials of a high enrichment with those of a lower enrichment. This degrades the quality of the material.

9. Critical configurations involving the smallest quantity of fissionable materials are those with finely dispersed materials in a hydrogenous moderator, such as water or organic materials. Particular attention should therefore be given to scrap solutions, sludges, cutting oils, degreasing agents, and similar substances which contain enriched materials.

10. The possibility of an operating or storage area becoming totally flooded with water should not be carelessly dismissed. Designs should include safety even under total inundation.

11. Allowance should be made for the possibility of operating personnel inadvertently bringing together two or more times the recommended amounts of fissionable material.

12. In general, nuclear safety should depend on not less than two concurrent unlikely events. For example, the minimum critical mass for U-235 in an optimum dispersion in water is approximately 800 grams. If, therefore, one were to maintain less than 400 grams of U-235 in a batch, a combination of double batching and

total dispersion would still not give rise to a nuclear incident.

Nuclear Safety

In the preparation of fuel elements, fissionable materials are most usually handled as massive metal. Scrap is normally in the form of solutions, suspensions, or dispersions, generally in hydrogenous media. Inasmuch as the treatment of these two forms of material is very different, they will be handled separately.

Massive Metal

In the handling of massive metal the following will serve as an approximate guide. A solid unreflected sphere of U-235 would be critical with a mass of approximately 50 kilograms. If it is totally reflected with light water, the critical mass is reduced by a factor of about two. Total of infinite water reflection is achieved with about 6 inches of light water. Thus, in the form of massive metal 20 kilograms of U-235 with sufficient physical separation can be stored with perfect nuclear safety, even allowing for inundation.

Hydrogenous Moderation

The moderation of fission neutrons is best effected by hydrogenous materials. For this reason systems containing hydrogenous materials require the least amount of fissionable material to sustain a chain reaction.

A. D. Callihan* has published an unclassified digest of nuclear safety as it pertains to solutions of fissionable materials. Some of the values are shown in Table I.

The values shown in Table I apply equally well to coolant or degreasing sludges, pickle liquors, or shavings kept under water or oil.

It should be made very clear that the values furnished in Callihan's table apply to aqueous solutions of light water in proximity to materials common in ordinary processing plants; water, concrete, stainless steel, etc., and that sizeable quantities of beryllium, graphite, heavy water, i.e., those materials which are superior to light water for the production of a chain reaction, are not present. Particular caution is indicated with respect to the volume, cylinder diameter, and slab thickness dimensions. These are only applicable to solutions having a concentration of 1 gram or less per cubic centimeter of the fissionable element. For example, the minimum critical slab thickness for U-235 in the form of metal is *considerably less* than the *1.4* inches listed above. In general, if the amount or configuration specified above is separated from similar quantities or geometries by a minimum of 2 feet, the system is completely safe regardless of treatment.

Practical use is made of this for storage arrangements in the so-called birdcage configuration, a schematic of which is shown in Fig. 2. The birdcage which is usually used is a 2′ x 2′ x 2′ cubical framework made up of rigid steel members. The container holding the fissionable material is positioned in the center of this configuration by means of structural supports similar to the frame. Usual construction provides that the framework be constructed of at least 2″ angles. The purpose of the configuration is to insure that the fissionable material can never be closer than two feet from the next storage package. Thus, if a safe quantity is placed in each container, a practically indefinite number of such containers can be stored in all directions. The materials are designed to withstand significant shock so that in the event of a transportation accident or other similar disaster occurrence, the integrity of the physical shape of the birdcage would be maintained.

TABLE I

Material	Mass (gm)	Volume (liters)	Cylinder Diameter (in.)	Slab Thickness (in.)	Concentration (gm/liter)
U-235 (90% enriched)	800	6.3	5.0	1.4	11.6
U-233	588	3.5	4.0	0.5	10.9
Pu-239	509	5.0	5.5	1.9	7.8

TYPICAL BIRD CAGE

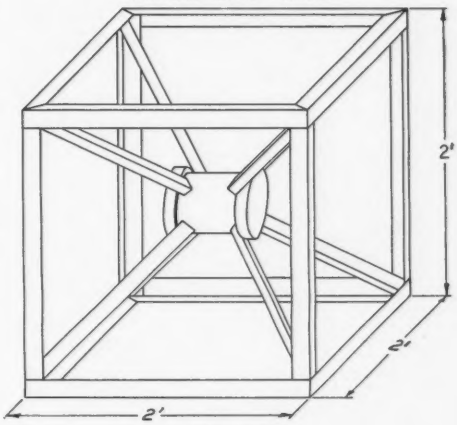


FIGURE 2

* Nucleonics, July 1956, V. 14, No. 47, p. 39.

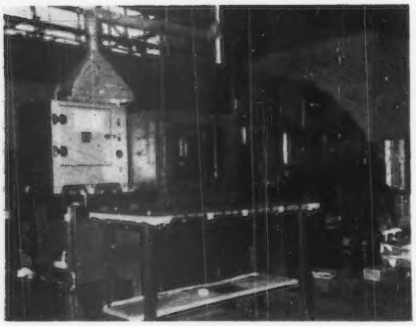


FIGURE 3.—Typical Equipment for Powder Production.

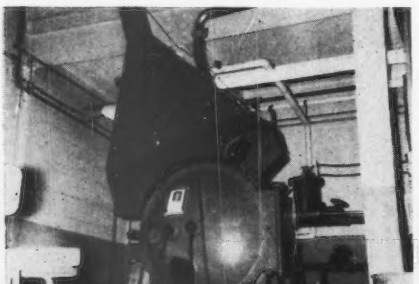


FIGURE 4.—Vacuum Induction Furnace showing ventilation provided for the opening of the furnace.

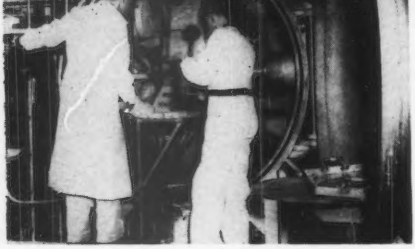


FIGURE 5.—Vacuum Furnace Power

Several photographs showing typical production equipment, and tables of occupational dust exposures during normal operations follow.

In Fig. 3 may be seen typical equipment for the production and handling of enriched powder. It is important to notice the size of the various pieces of equipment. This is made necessary by limitations imposed on quantity by considerations of nuclear safety. The oven, which may be seen to the left of the photograph, is protected by the exhaust ventilation port above the door opening and further protected against spillage by means of a stainless steel tray in which the oven is set. The press which is in the center of the photograph is completely enclosed, with a door in the front, and is ventilated through the rear and side with further exhaust connections. The glove box shown at the right of the photograph is also exhausted.

In Fig. 4 is shown a typical installation of a vacuum induction furnace. This furnace is equipped with a peripheral exhaust hood which sweeps air across the face of the furnace when the furnace is open. A flexible hood connection is also provided for more local ventilation.

Fig. 5 shows the pouring of an enriched ingot. The size of the mold and the size of the crucible indicate the severe restrictions placed on this type of operation by nuclear safety require-

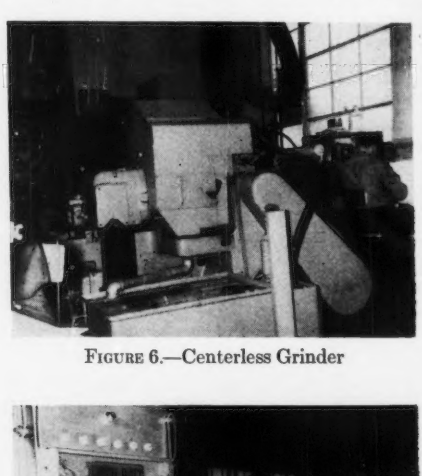


FIGURE 6.—Centerless Grinder

FIGURE 7.—Muffle Furnace for Heating "Sandwiches."

ments. Directly above the pour is positioned an exhaust duct which carries any fumes produced in the pour away from the operator.

A typical high speed operation may be seen in Fig. 6. Here we have a centerless grinder which is completely enclosed except for small introduction and exit ports. The large flexible exhaust duct seen in the top right-hand section of the photograph indicates the quantity of air which must be exhausted from even as small a machine as this one where high speed grinding is being done.

After the enriched ingot has been solidified, it is clad with an inert material. In Fig. 7 is shown a part of the procedure for jacketing the enriched material with aluminum. The muffle furnace which is shown at the left-hand side of the photograph contains "sandwiches" with enriched "meat" and an aluminum exterior. It is possible to see the type of spacing which is used within the furnace to provide for criticality. The scale of operations can be seen from the size of the rolling mill shown at the right.

In Table II is shown individual occupational exposures during the handling of material of three different degrees of enrichment. It must be pointed out that the operations involving these three different kinds of material are not truly comparable, but the data do give some indication of the influence of the type of cladding and the degree of enrichment on air concentration. Uranium-Zirconium alloy appears to create less airborne material than equivalent concentration alloys with other materials. Fully enriched material can result in serious air contamination as is seen by the value for cleaning powder handling equipment. Even clad, fully enriched material, while it is being rolled can result in significant concentrations in the air.

TABLE II

Operational Exposures d/m/M³

25 w/o U-Zr (Unclad)		90 w/o Uranium-235	
Handling Pieces	25	Hot Cladding	320
Cleaning and Assembling Furnace	75	Cutting-Clad	40
Removing Ingot	50	Loading Retort (Glovebox)	250
Hammering	80	Powder Handling (Glovebox)	3500
3.5 w/o-U-Th (Oxides)			
Weighing and Pelletizing	15	Cleaning Powder Handling Equipment	13000
		Rolling-Clad	1000
		Cutting and Milling	700
		Stripping Cladding	2700

TABLE III

Operational Exposures 5 w/o U-Al d/m/M³

Clad Alloy		Unclad Alloy		Founding Raw Alloy (Ventilated)	
Hacksaw Jackets	370	Sandblast (cabinet)	450	Feeding Stock	130
Hammering Jackets	70	Degreasing	400	Removing Dross	15
Opening Jackets	4500	Weighing	200	Pouring	120
Rolling	60	Punching	400	Cleaning Furnace	35
Milling	5	Shearing	20		
Punching	15	Brushing (glovebox-unventilated)	250		
Extrusion	50				

TABLE IV

Daily Average Exposure of Production Operators-d/m/M³

U-Al (5 w/o)	
Furnace Operator	6
Rolling Operations (Clad)	4
Vault Operations	10
U- >90 w/o	
Powder Preparations	400
Rolling Operations	400
Milling and Cutting	500

In Table III may be seen the occupational dust exposures for comparable operations on comparable materials. In each case the operations herein presented were performed on a 5% uranium alloy in aluminum. In general, during operations on clad materal, exposures are well within levels specified as permissible. With operations on the unclad material, on the other hand, concentrations are of the order of, or greater than, permissible by a factor of about 2 to 5. Ventilation provides satisfactory control even on hot operations as may be seen in the third column.

In Table IV are listed the daily average exposures of production operators to similar types of operation with the only difference being the per cent of enrichment. As can be seen from this table, a difference of approximately a factor

TABLE V

Daily Average Exposure of Production Operators —Miscellaneous Materials d/m/M³

Fuel Element Production	160
Pickling Parts	90
Furnace Operator	15
Extrusion Operator	15
Vault Operations	60
Finished Product Area	80

of 100 may be expected between the 5% material and the 90% enriched uranium.

In Table V is listed the daily average exposures of several people involved in production operations on various types of material. Here the enrichment, alloying and cladding varied from batch to batch. Most of the operations are satisfactorily within the maximum permissible concentration, but certain of the operators appear to be occasionally overexposed.

The handling of enriched uranium in the production of fuel elements poses several unique problems. The solutions to these problems are not greatly different from normal industrial practice, but the care that must be employed to insure safety goes beyond anything which industry normally uses. It is significant to note that despite the unusual nature of the controls which are required, there has never been an accident wherein the handling of enriched uranium materials has resulted in injury. It is to be hoped that the precautions which will be exercised during the necessarily extensive growth of the program will be sufficient to maintain this excellent record.

Acknowledgments

The authors should like to express their thanks to Metals and Controls, Inc. and Babcock and Wilcox, Inc. for their cooperation and for making available the photographs of the processing apparatus exhibited.

They acknowledge the help of their colleagues in the Industrial Hygiene, Analytical, and Instruments Branch of the Health and Safetly Laboratory who contributed in great measure the details of measurement upon which this paper is based.

A.C.G.I.H. Manual of Analytical Methods

The American Conference of Governmental Industrial Hygienists has prepared a *Manual of Analytical Methods* for the sampling and analysis of atmospheric contaminants. This Manual contains eleven procedures which have been critically tested and evaluated by a referee-collaborator system, conducted by the Conference's Committee on Recommended Analytical Methods. The procedures are offered as a loose-leaf binder collection to facilitate the addition of future methods as they become available upon approval of the Committee.

The methods now available include procedures for arsenic, chlorinated hydrocarbons, formaldehyde, hydrogen sulfide, lead, manganese, mercury, oxides of nitrogen, parathion, and sulfur dioxide. Two methods for sulfur dioxide are offered: one is a fuchsin-formaldehyde procedure, the other a polarographic method. A dithizone method for cadmium has been tested and approved but its manuscript has not been subjected to final editing.

The price of the Manual is $5.00 and includes the cadmium procedure and eight additional methods as they become available. Orders for this Manual should be addressed to Mr. C. D. Yaffe, Secretary-Treasurer, A.C.G.I.H., 1014 Broadway, Cincinnati 2, Ohio.

The Effectiveness of Sand as a Filter Medium

R. E. YODER AND F. M. EMPSON

Oak Ridge National Laboratory, Oak Ridge, Tennessee*

IT HAS BEEN demonstrated at the Oak Ridge National Laboratory and elsewhere[1, 2] that an aerosol size for maximum penetration exists for many filter materials. One can now design a filter made of the media for which the penetration characteristics are known and secure any degree of protection desired for all aerosols.

At the Oak Ridge National Laboratory sand filters have been studied under a variety of conditions to determine their usefulness as a filter medium for aerosols in low velocity air streams.

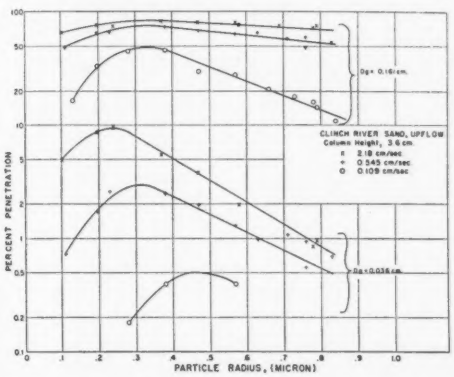


FIGURE 1. Aerosol Penetration through Dry Sand

Experiments have been performed using sand as a filter media under two basic conditions:

(1) The use of sand filters to remove aerosols from dry or low humidity air streams.

(2) The use of sand filters to remove aerosols from water saturated or high humidity air streams.

Homogeneous DOP (di-octyl-phthalate) aerosols were used to test the sand filters in low humidity air streams. The aerosols were produced in a La Mer type thermal aerosol generator and detected by a revised NRL smoke penetrometer.[3, 4] The particle size of the aerosol could be varied to produce homogeneous aerosols of any size in the 0.1–1.0 micron radius range. Also, polystyrene latex microspheres of 0.58, 0.41, 0.27, and 0.25 micron radius, were atomized and used as solid aerosols.†[5] There was no measurable difference in the penetration of the liquid DOP and of the solid polystyrene.

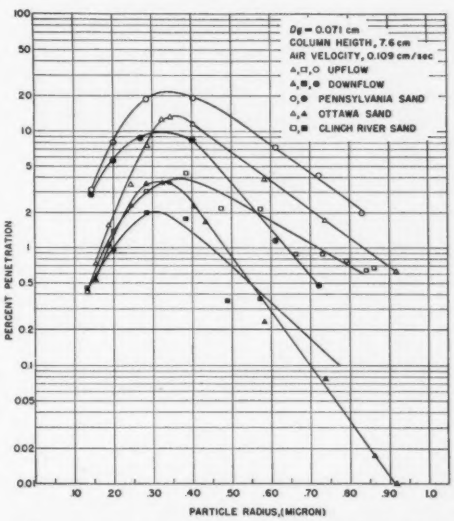


FIGURE 2. Aerosol Penetration through Three Types of Dry Sand

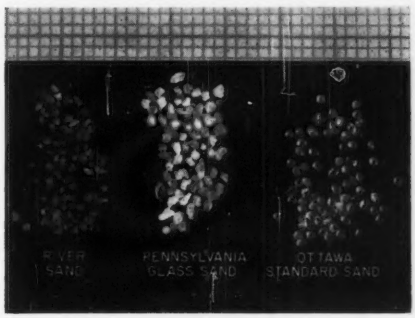


FIGURE 3. Sand Grain Structures

The data presented in Figure 1 show that

* Oak Ridge National Laboratory is operated for the Atomic Energy Commission by the United Carbide Nuclear Company.

† Supplied through the courtesy of Dow Chemical Company, Midland, Michigan.

there exists an aerosol size for maximum penetration and that the aerosol size for maximum penetration decreases as the aerosol velocity increases. The filter penetration is dependent upon the sand grain size, the smaller grained sand being more effective as a filter than the larger grained sand.

Three types of sand were used, Figure 2, to determine the effect of sand grain shape on the filtration efficiency of sand. The three sands used were a local river sand, Ottawa Standard Testing Sand (through 20-retained on 30 mesh, for ASTM Test ⅌C-190), and a sharp grained sand referred to as Pennsylvania Glass Sand. The local river sand is more effective than either of the other sands. Filtration efficiency is also greater when the aerosol stream passes down through a filter rather than up through the filter. Figure 3 is a photograph of the three types of sand used in our experiments.

The first tests of sand as a filter medium for air saturated with water vapor consisted simply of boiling a dilute solution of $Au^{198}Cl$ and passing

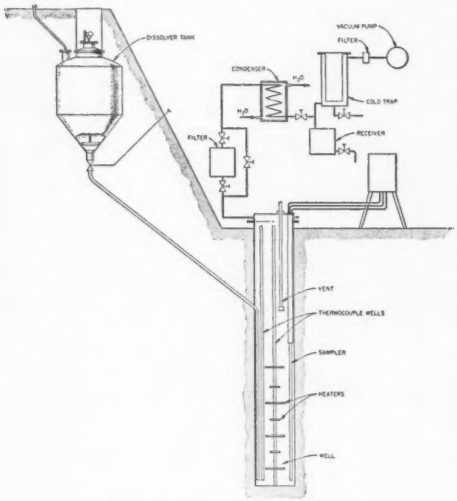


FIGURE 4. Entrainment Well

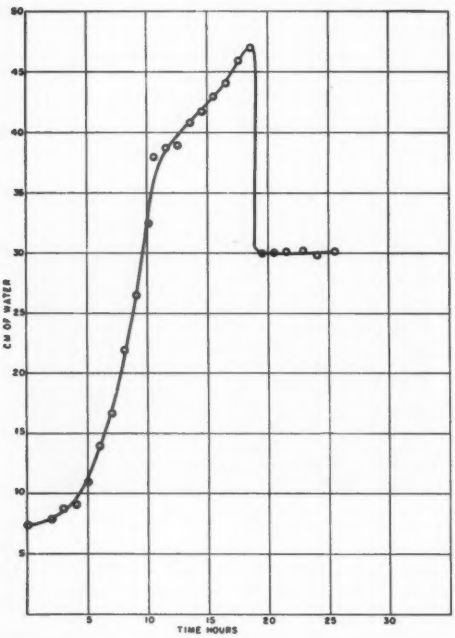


FIGURE 5. Pressure Drop across Sand Filter

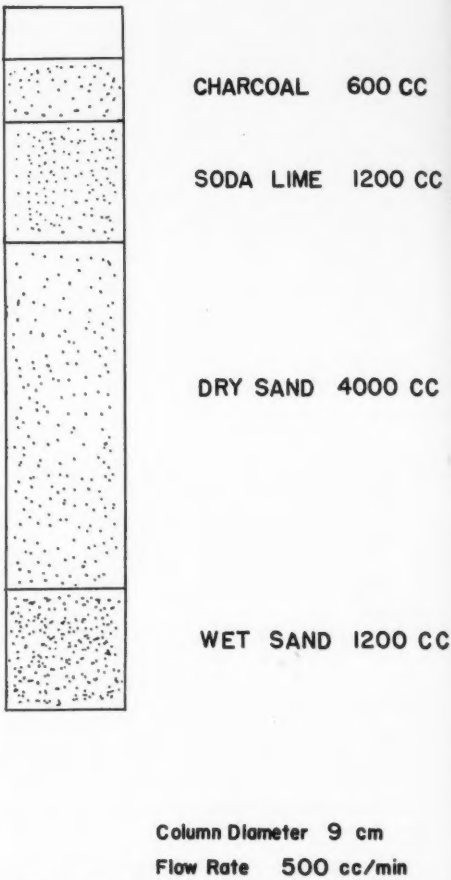


FIGURE 6. Multibed Low-Velocity Air Cleaner

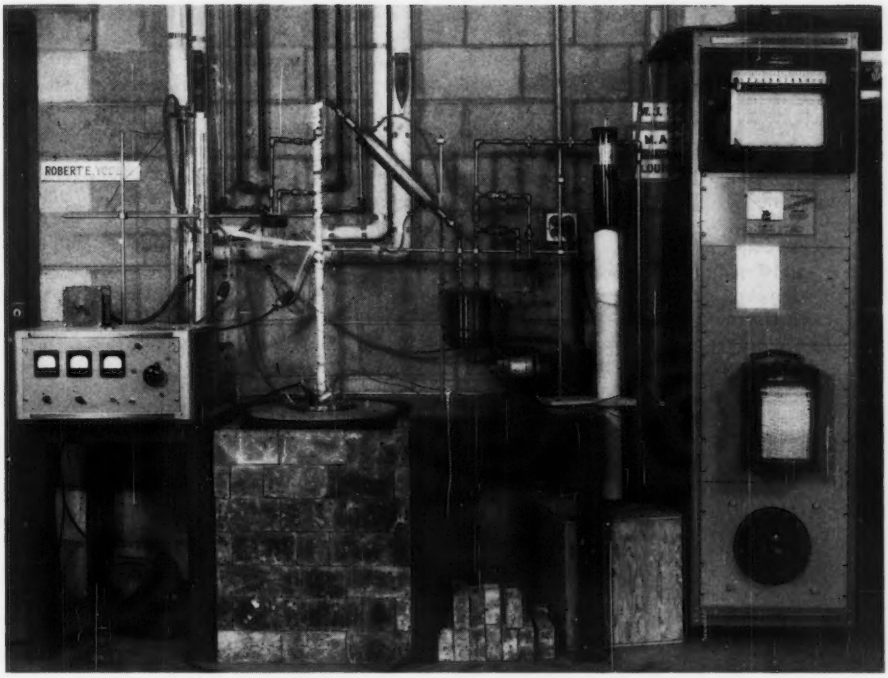


FIGURE 7. Multibed Air Cleaner in Test Equipment

the resulting aerosol through a bed of the sand under test. The equipment for these tests is shown in Figure 4. The vapor passing through the filter was condensed and the condensate counted by standard radiometric procedures. For comparison the vapor stream was passed through a by-pass to the condenser directly without having been filtered.

It was found that the sand filter bed functions as a condenser, with the water collecting in the voids and plugging the filter. The pressure drop across the filter gradually rises as the bed is filled with water until channels form in the sand allowing the aerosol to pass through the filter without being filtered, Figure 5. This condition occurs after a sufficient quantity of moisture laden air has passed through the filter to deposit enough water to fill completely the voids in the sand. The void fraction, or the ratio of the interstital volume to the total volume, of all sands used was approximately 0.38.

At about the time this information was obtained, a fume and radioactivity containment problem arose in connection with the waste disposal program of the Health Physics Division at the Oak Ridge National Laboratory. It was proposed that a waste solution containing large quantities of radioactivity be sintered with shale, soda ash, and limestone as additives to form a ceramic mass which would retain essentially all the radioactivity of the waste solution. During this sintering operation, the water contained in the waste solution would be vaporized, followed by the evolution of oxides of nitrogen. It was desired that the water vapor, the oxides of nitrogen, and the entrained radioisotopes be contained as completely as possible.

TABLE I

Sand Filters Radioactive Particulate Studies

Radioactive Isotope	Activity Evolved	Activity in Condensate	Activity in Sand Filter	Activity in Scrubber
Iodine	100%	80%	20%	0%
Ruthenium	100%	90%	10%	0%

A filter and adsorber was designed to perform this function, Figure 6. It consists of a bed of sand, supporting a small bed of soda lime, and a small bed of activated carbon. This sand bed has a volume sufficiently large to hold in the

first few inches of sand all moisture which will condense during the life of the filter. The remainder of the sand will continue to function as a filter without excessive pressure drop. This sand bed is designed with sufficient sand depth to remove particulate matter to the extent required. The soda lime and activated carbon are designed to prevent the escape of nitrogen oxides, and iodine. If equipment is arranged so that condensed water vapor can drain into a sump below the filter bed, a smaller volume of sand will be required for condensation and condensate holdup, Figure 7.

This method of filtration has been tested on an aerosol containing radioactive ruthenium and iodine, together with water vapor and oxides of nitrogen. Ruthenium was not found in the air stream which passed through the filter. Iodine condensed and resublimed on the sand filter, gradually working its way to the interface of the sand and soda lime. The performance of the compound filter is shown in Table I. The iodine was largely present at the sand soda lime interface. Some oxides of nitrogen passed through the soda lime and were found in the offgases. However, the addition of 4 inches of activated carbon retained the oxides of nitrogen.

In conclusion we feel that, with proper filter design, sand may be used to filter aerosols from either dry or moist gas streams. Ruthenium and iodine have been successfully removed from the vapor stream arising from a boiling mixture containing each of these isotopes.

References

1. Thomas, J. W., and Yoder, R. E., Aerosol Size for Maximum Penetration through Fiberglas and Sand Filters; *Archives of Industrial Health; 13:* 545, 1957.
2. Fitzgerald, J. J., and Detwiler, C. G., Optimum Particle Size for Penetration through Millipore Filter, *Archives of Industrial Health; 15:* 3, 1957.
3. Grassel, E. E., Construction of a La Mer Type Thermal Aerosol Generator for Radioactive Compounds, ORNL-CF-54-3-46. April 13, 1954.
4. Knudson, H. W., and White, L., Development of Smoke Penetration Meters, Report P-2642, Naval Research Laboratories, September 1954.
5. Engquist, E. H., Preliminary Design Calculations for Filter Material Tests with Radioactive Dusts, Report AD-159 (H), Naval Radiological Defense Laboratory, September 14, 1949.

Manual of Uniform Definitions of Home Accidents*

This manual of definitions was drawn up by the Conference on Uniform Definitions of Home Accidents that met in Chicago, April, 1957. While not designed as a dictionary or glossary, the booklet supplies precise meanings of terms in the home-accident field and should prove useful to all personnel engaged in home-accident reporting or home-accident prevention programs. Criteria employed in the manual include the following: (1) the term must be pertinent home-accident prevention; (2) it must have a special connotation in home-accident prevention or a related field (medicine, statistical analysis, engineering, etc.); (3) it should if possible indicate measurable variables. Certain terms in common usage which are subject to misinterpretation are included in the manual but clearly defined common or nontechnical terms found in the average dictionary are omitted. Communications concerning the definitions should be addressed to the National Office of Vital Statistics, Public Health Service, Department of Health, Education, and Welfare, Washington 25, D.C.

* Conference on Uniform Definitions of Home Accidents (sponsored by the Public Health Service, the American Public Health Association, and the National Safety Council), Public Health Service Publication No. 577, for sale by the Superintendent of Documents, U.S. Government Printing Office, Washingtin 25, D.C.—Price 30 cents.

Criteria for Establishing Short Term Permissible Ingestion of Fallout Material

GORDON M. DUNNING

Division of Biology and Medicine Atomic Energy Commission, Washington, D. C.

THE CRITERIA for establishing permissible ingestion of radioactive fallout material under emergency conditions for several weeks following a nuclear detonation are dependent primarily on exposures to the,

a. gastrointestinal tract from the gross fission product activity,

b. thyroid from the isotopes of iodine and,

c. bone, principally from Sr^{90}-Y^{90}, Sr^{89}, Ba^{140}-La^{140}.

I. Doses to the Gastrointestinal Tract

The following principal assumptions are used in calculating the doses to the gastrointestinal tract of adults:

a. The calculations are based on the methods contained in reference one.

b. The fallout material is 90 per cent insoluble. (See IV. Discussion below).

c. The activity decays according to the principle of $(\text{time})^{-1.2}$.

d. The energy delivered is all derived from the beta emissions, having a mean energy of 0.4 Mev when in the lower large intestine. (See Graph 1)[2]

e. The total daily consumption of food and water is 2200 grams or milliliters.

The method of calculation is according to the following equation:

$$\frac{\text{(Total number of disintegrations occurring in organ) (Energy of emissions) } (8.0 \times 10^{-9})}{\text{Mass of Organ}} = \text{Dose (rads)} \quad (1)^*$$

The number of disintegrations taking place in the organ may be calculated according to equation two:

$$\text{Total number of disintegrations} = 5A_a\, t_a^{1.2}[t_a^{-0.2} - t_b^{-0.2}] \quad (2)$$

Where: A_a = number of disintegrations per unit time at time "a" after detonation.

t_a = time "a" after detonation.

t_b = time "b" later than "a".

One of the more useful forms for the criteria would be in units of permissible concentrations at time of intake. This will somewhat complicate the calculations since there will be a decrease in activity as the material passes along the gastrointestinal tract. When such calculations are made according to the above assumptions and equations, it may be seen that the critical organ is the lower large intestine except for the first hours immediately following the detonation. (Table I shows the relative doses to parts of the gastrointestinal tract as a function of time.) Therefore, Graph 2 is based on the activity at time of ingestion to produce one rad of dose to the lower intestine.

For example, Graph 2 shows that if about 48 microcuries are ingested on the 24th hour after detonation, the lower large intestine may receive one rad of radiation dose. This was calculated in the following manner.

Step 1. Determine the total number of disintegrations in the lower large intestine necessary to produce 1.0 rad.

From equation (1)

$$\frac{\text{(Number of disintegrations) } (0.4)\ 8.0 \times 10^{-9})}{150} = 1$$

Number of disintegrations $= 4.7 \times 10^{10}$

Step 2. Determine the activity at time of intake to produce 4.7×10^{10} disintegrations within the large intestine.

$\frac{4.7 \times 10^{10}}{0.9} = 5.2 \times 10^{10}$ disintegrations intake required (assuming 10% solubility).

From equation (2)

$$5.2 \times 10^{10} = (5)\ (A_{37})\ (37^{1.2})\ [37^{-0.2} - 55^{-0.2}]\ *$$

$A_{37} \cong 3.7 \times 10^9$ d/hr.

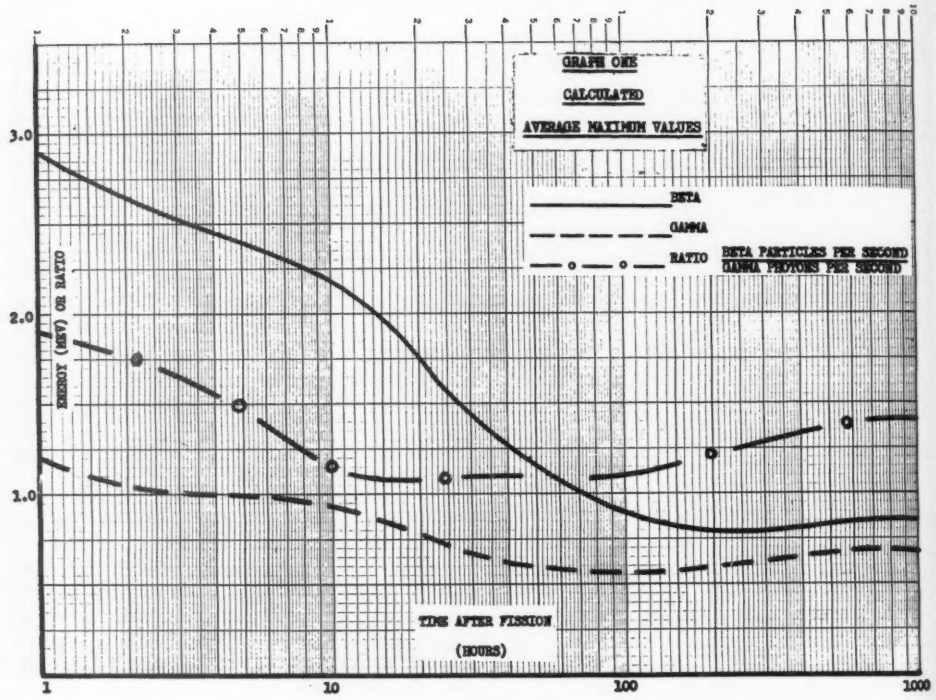
$A_{24} \cong 6.2 \times 10^9$ d/hr.

$A_{24} \cong 47\ \mu c$

* The rad is the unit of absorbed dose equal to 100 ergs per gram.

$$\frac{1.6 \times 10^{-6}\ \text{(ergs/Mev)}\ 0.5\ \text{(proportion of total energy to gastrointestinal tract)}}{100\ \text{(ergs/gm-rad)}} = 8.0 \times 10^{-9}$$

* If the time of intake is the 24th hour, then the start of irradiation of the lower intestine is 24 + 13 = 37th hour, according to reference one.



GRAPH 1

TABLE I

Relative Doses to Gastrointestinal Tract from Ingestion of Fallout Material

	Time After Detonation That Ingestion Occurs		
	1st Hour	1st Day	Limiting Case*
Lower Large Intestine	1.0	1.0	1.0
Upper Large Intestine	1.3	0.71	0.49
Small Intestine	0.26	0.054	0.03
Stomach	0.86	0.063	0.03

* Based on assumption that there is no significant decrease in activity during time of passage through gastrointestinal tract. After a week following detonation the decrease in activity between the stomach and the midpoint of time in lower large intestine is within about 20%of this condition.

Graph 2 has been used in estimating radiation doses to the lower large intestine for prolonged periods of ingestion (Table II). The following calculations are illustrative for the period of 24th to the 120th hour (start of intake at the beginning of the 2nd day after detonation for a duration of four days).

Step 1. Determine the number of microcuries at time of ingestion to produce 1.0 rad to the lower large intestine.

From Graph 2 take the mid point of intake period (72nd hour) $\rightarrow$ 31 μc. (This is obviously an approximation since the exact times of intake during the four-day period will be unknown.)

Step 2. Determine the activity at time of intake.

From equation (2)

$31 = 5A_{24}\ 24^{1.2}\ [24^{-0.2} - 120^{-0.2}]$

$A_{24} \cong 0.94\ \mu$c/hr

Since there is assumed a 2200 ml/day intake

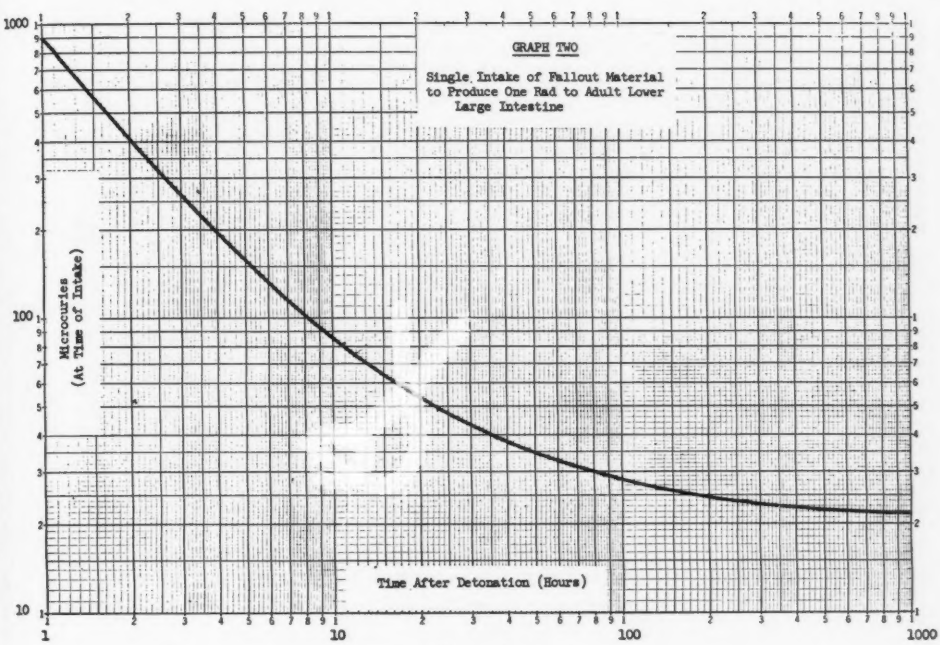
$$0.94 \times \frac{24}{2200} \cong 0.010\ \mu\text{c/ml or gm}$$

II. Doses to the Thyroid

The following principal assumptions are used in calculating the doses to the adult thyroid from intake of activity from fallout material:

a. The percentages of the isotopes of iodine in mixed fission products are according to Hunter and Ballou.[3]

b. Twenty percent of the ingested I^{131} reaches the thyroid.



GRAPH 2

c. The mean energy is 0.22 Mev.

d. The thyroid weight is 20 grams. (See IV. Discussion below)

e. The percentages of shorter-lived isotopes of iodine that reach the thyroid and their doses are according to reference four.

The method of calculation of doses to the thyroid is illustrated by computing that amount of intake of fission products at the 48th hour to produce 1.0 rad.

Step 1. Determine the dose rate on the day of intake of I^{131} to produce 1.0 rad to the thyroid.

$D = (R/\lambda_e)$

Where: D = dose (1.0 rad)
R = dose rate on initial day
λ_e = effective decay constant (radiological and biological)

$1.0 = (R/0.09)$

$R = 0.09$ rads/day

Step 2. Determine the number of microcuries of I^{131} to produce 0.09 rad/day

$$\frac{X(\mu c)(2.2 \times 10^6)(60 \times 24)(1.6 \times 10^{-6})(0.22)}{(100)(20)} = 0.09$$

$X = 0.16$ μc to thyroid or

(0.16) (5) = 0.80 μc I^{131} ingested

Step 3. Determine relative doses from I^{131} and I^{short} according to Graph 3.[4]

TABLE II

Approximate Fission Product Activities (Microcuries per Milliliter of Gram $\times 10^2$) to Produce one Rad Dose to Lower Large Intestine*

Duration of Ingestion (Days)	Start of Intake (Days after detonation)							
	1 (1st Hour)	2 (24th Hour)	3	4	5	10	15	20
1	35	2.5	1.9	1.7	1.4	1.1	1.1	1.0
2	24	1.7	1.1	0.89	0.81	0.62	0.57	0.53
3	15	1.3	0.82	0.65	0.56	0.41	0.40	0.37
4	13	1.0	0.65	0.53	0.46	0.33	0.30	0.29
5	12	0.9	0.57	0.44	0.39	0.28	0.25	0.22
10	9.2	0.64	0.40	0.29	0.25	0.17	0.14	0.13
15	7.8	0.53	0.33	0.26	0.21	0.13	0.11	0.097
20	7.5	0.49	0.29	0.21	0.18	0.11	0.089	0.079

* a. Activities computed at start of intake period.

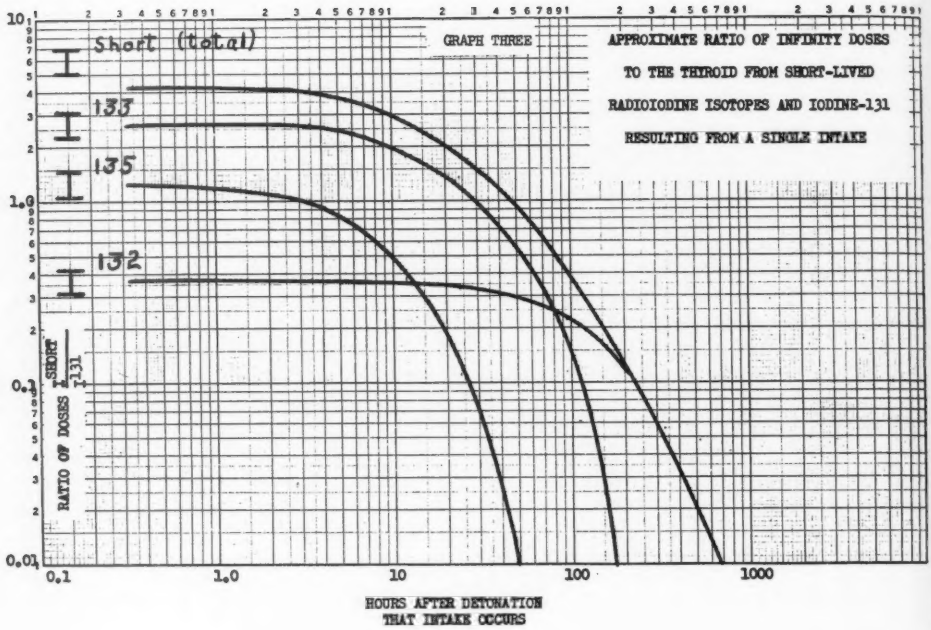
b. Based on intake of 2200 milliliters or grams of water and food per day for adults.

At 48th hour, the relative contribution to total dose from I^{131} and I^{short} is about 1/1.

Therefore, ingestion of 0.4 μc I^{131} (equivalent) at 48th hour will produce 1.0 rads to thyroid.

Step 4. Determine the number of microcuries of fission products required to yield the required I^{131} activity. At 48th hour, I^{131} constitutes about 2.35% of total activity. Therefore,

(0.4/0.023) $\cong$ 17 μc of fission products.



GRAPH 3

Graph 4 shows the number of microcuries of fission products ingested at times after detonation to produce 1.0 rad to the thyroid.

III. Doses to the Bones

The three principal bone-seeking isotopes of concern are Sr^{90}-Y^{90}, Sr^{89}, and Ba^{140}-La^{140}. Evaluation of these may be made in terms of amount deposited in the bones versus maximum permissible body burdens, or in rads of dose that they deliver after deposition. Since values for maximum permissible body burdens are based on the concept that these will be maintained indefinitely in the body, they are not so valid for Sr^{89} and Ba^{140}-La^{140} when considering short periods of emergency intake.

The following principal assumptions are used in calculating the doses to the bones of adults:

a. The percentages of the isotopes of Sr^{90}-Y^{90}, Sr^{89}, and Ba^{140}-La^{140} in mixed fission products are according to Hunter and Ballou.[3]

b. The percentages of intake of these isotopes that are deposited in the bones, the energies of emissions, and their effective half lives are according to reference five—except for Sr^{90} where a 27.7 year radiological half life is used here.

c. The mass of the bones is 7,000 grams.

The method of calculation of doses to the bones is illustrated by computing the dose from Sr^{89} from the intake of 27 microcuries (See IV Discussion below) of mixed fission products on the 120th hour. Similar calculations were made for Sr^{90}-Y^{90} and Ba^{140}-La^{140} and then the three doses were added for each intake of fallout material.

Step 1. Determine the Sr^{89} to reach the bone.

According to reference 4:

The Sr^{89} content in mixed fission products on the 120th hour is 1.6%.

According to reference 5:

The intake of Sr^{89} to reach to the bones is 25%.

Therefore:

(27) $(0.016)(0.25) = 0.108$, to the bone.

Step 2. Determine the dose rate to the bones.

With an assumed effective energy of 0.55 Mev (reference 5):

$$\frac{(0.108)(2.2 \times 10^6)(60 \times 24)(1.6 \times 10^6)(0.55)}{(100)(7{,}000)}$$

$$= 4.3 \times 10^{-4} \text{ rads/day } \textit{or } 0.43 \text{ millirads/day}$$

Step 3. Determine total dose.

D total $= (R/\lambda e)$

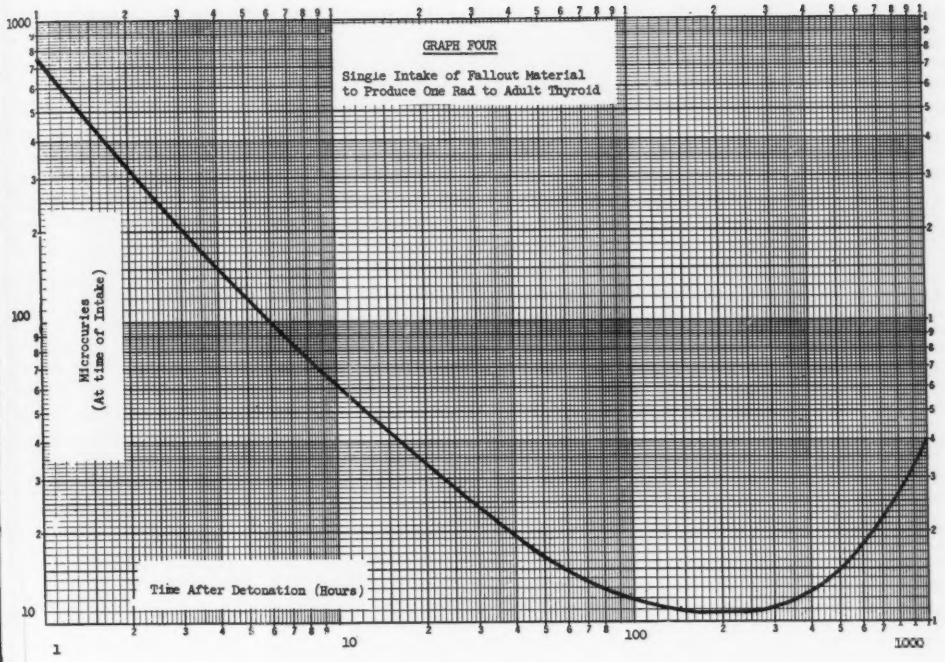
where: R = initial dose rate

λe = effective decay constant

D total $= (0.43/0.0133) \cong 32$ millirads*

* The relative total doses from these isotopes are as follows:

Time of intake	Sr^{90}	Sr^{89}	$Ba^{140} - La^{140}$
24th hour	0.6	1.00	0.6
20th day	1.00	1.00	0.3



GRAPH 4

IV. Discussion

A. SOLUBILITY

The solubility of fallout material varies, depending among other factors upon the surface over which the detonation occurred. The fallout material collected in soil samples at the Nevada Test Site has been quite insoluble, i.e. only a few per cent in distilled water and roughly 20–30 per cent in 0.1 N HCl. However, it would be expected that the activity actually present in drinking water supplies would be principally in soluble form. The water collected from a well and a cistern on the Island of Rongelap (Table III) about 21 months after the March 1, 1954 fallout, was found to have about 80 per cent of the activity in the filtrate, but there was an undetermined amount that settled to the bottom. Other data suggest the material to have been about 10–20 per cent soluble in water.

In the event contaminated food is ingested it is possible that the total activity—soluble and insoluble—may find its way into the gastrointestinal tract since at times immediately following a fallout most of this activity probably would come from the surface contamination rather than the soil-plant-animal cycle. There may then follow some solubilizing in the acid stomach with subsequent removal from the tract before reaching the lower large intestine.

TABLE III

Concentrations in Water on Islands in the Pacific and Estimated Gamma Dose Rates at D + 1, Three Feet Above Ground

Date	Location	Gross Fission Product Activity (*d/m/ml*)
	Rongelap Island (3.5 roentgens per hour)	
D + 2	Cistern	~50,000–75,000
D + 34	"	~5,500
D + 34	Openwell	~2,000
D + 300	Cistern	~3
D + 330	"	~4
D + 600	"	~5.5
D + 600	Openwell	~0.5
D + 600	Cistern (With collapsed roof)	~1.3
	Kabelle Island (19 roentgens per hour)	
D + 330	Ground water	~48
	Eniwetok Island (8.5 roentgens per hour)	
D + 330	Cistern	~25
	Enibuk Island (1.3 roentgens per hour)	
D + 600	Standing water from can, drum, etc.	~1.4

It is assumed for these calculations that (a) 90% of the fallout material is insoluble when computing doses to the gastrointestinal tract, and (b) that the isotopes of iodine, strontium, and barium are all soluble when computing doses to the thyroid and to the bones. These assumptions are probably conservative, i.e. they may overestimate somewhat the radiation exposures.

B. Biological Significance

After the estimation of radiation doses by any procedure the final step is an evaluation in terms of biological effects both for short and long terms.

1. Gastrointestinal Tract

There have been few experiments where the gastrointestinal tract has been exposed in a manner similar to the one assumed here. One experiment[6] indicates lower doses to the intestine than the model proposed in reference 1.

In another experiment,[7] rats were fed 1.0 to 6.0 millicuries of yttrium-90 in a single feeding. Four of the 33 animals died of adenocarcinoma of the colon and additional animals died with acute and chronic ulceration of the colon. A second group of rats was given 0.46, 0.20, or 0.06 mc of Y^{91} per feeding over a period of three months with total accumulated amounts of 31.2, 15.6 and 4.68 mc respectively. Six of the eight animals at the two higher levels died with carcinoma of the colon and no malignancies were observed at the lowest level. The authors made no estimate of radiation doses.

In another experiment,[8] rats were kept alive by the use of parabiosis or para-aminopropriophenone either pre or post whole-body irradiation of 700–1000 roentgens. Four of the 21 rats developed tumors along the gastrointestinal tract (one each jejunum, ileum, duodenum, and colon), with four additional animals showing tumors in other organs. However, in comparing gastrointestinal versus whole-body irradiation, the question has been raised as to a possible indirect carcinogenic action in the latter case.[9] By using fast neutrons, lesser doses have been shown to produce an appreciable percentage of intestinal carcinomas in mice, but this is not so relevant to the present discussion of beta exposure.[10]

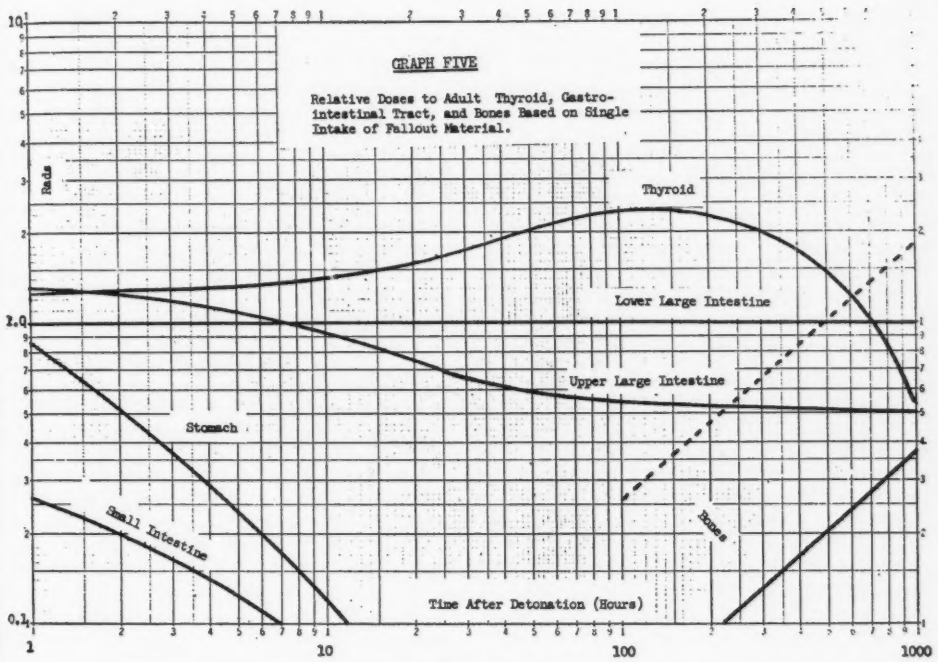
One summarizing statement of the short-term effects stated, "... though the gastrointestinal tract is one of the sensitive systems to ionizing radiation, it also has a most remarkable regenerative and reparative capacity. It takes doses of well over a thousand roentgens to damage the gut permanently in most mammals studied, and it is capable of rapid, dramatic recovery of anatomical and functional integrity with doses in the lethal range."[11] Evaluating the data from dogs exposed to whole-body X-radiation the authors said, "... it is suggested that doses of approximately 1,100 to 1,500 r may represent the upper limit of the possible efficacy of supportive measures in the treatment of the syndrome of acute radiation injury. With greater doses the damage to the intestinal mucosa appears irreparable and of an extent incompatible with life."[12] At the same time, it has been repeatedly indicated that the irradiation of the gastrointestinal tract plays a major role in gross whole-body effects associated with radiation syndrome.[11, 12, 13, 14, 15, 16, 17, 18, 19, 20] In fact one author[13] summarizes several experimental findings, "In producing acute intestinal radiation death, irradiation of any major portion of the exteriorized small intestine alone is almost equivalent to whole-body irradiation ...."

Graph 5 suggests the relative doses to the parts of the gastrointestinal tract, from ingestion of fallout material. The available experimental data does not permit a conclusive statement as to whole-body effects to be expected from such ratios of exposures. Most of these experiments are related to the criterion of death, but they do suggest that the major contributory factor to such effects such as nausea and vomiting associated with whole-body exposures of 100–200 roentgens, may be the result of the gastrointestinal reaction. Possibly a few hundred rads to the lower large intestine together with the concomitant lesser exposures to the upper large intestine, the small intestine and the stomach (according to Graph 5) may be in the range where radiation sickness might occur.

2. Thyroid

The study and treatment of disorders of the thyroid gland with radioiodine has led to considerable information on doses and their effects to this organ. (Only a partial list of references is noted.)[21, 22, 23, 24, 25] Whereas these treatments have been principally with abnormal thyroids, much of the information may be extrapolated to normal thyroids for the purposes of this discussion. In addition there are other data based on normal thyroids in patients suffering such ailments as congestive heart failure.[26]

The picture clearly presented is that the adult human thyroid is relatively insensitive to radiation. For example, Freedberg, Kurland, and Herman,[26] report, "... Seven days after administration of 17 and 20 millicuries of I^{131}, which delivered 14,500 and 31,000 rep, respectively, to the thyroid gland, no histologic



GRAPH 5

changes were noted which could be attributed to I^{131}.... Fourteen and twenty-four days, respectively, after administration of 59 and 26 millicuries of I^{131}, marked central destruction of the thyroid gland was noted...." Since the first two patients expired seven days after administration of the I^{131} from pulmonary edema, it does not eliminate the possibility that the destructive changes might have appeared in the thyroid if these patients had survived. However, the evidence from other studies strongly indicates that if any pathological effects were to be noted in the thyroid after an exposure of some 10,000 reps they would be minimal. Likewise, the possibility of serious damage to other organs of the body, such as parathyroids and trachea which are simultaneously exposed to the I^{131} radiations, would be exceedingly small.

On long terms effects, two summarizing statements may be made. "No thyroid neoplasm was found which could be attributed to I^{131},"[26] after doses to normal thyroids running into many tens of thousands of reps and after periods of observation up to more than eight hundred days. "In a series of over 400 patients treated with radioactive iodine at the Massachusetts General Hospital during the past ten years no known carcinoma of the thyroid attributable to this agent has developed. Definite answers to the question of carcinoma formation must await prolonged observation of treated patients."[23] Here the average treatment dose of I^{131} was 10 millicuries and of I^{130} 25 millicuries.

However, significantly lesser doses may be carcinogenic in children.[27] "...It has been suggested that the human thyroid is less radiosensitive than other tissues, such as bone, since after many years of treatment of Graves' disease with radioactive iodine, no cases of resulting carcinoma have been reported. The customary dosages of I^{131} in such cases yield at least 4000 rep to the gland. On the other hand, carcinoma of the thyroid found in children and young adults has almost invariably been preceded by x-ray treatment to the upper part of the body, in amounts such as to yield as little as 200 r to the infant thyroid. It has been estimated that less than 3 per cent of such treated cases yield carcinoma; nevertheless, the data suggest that 200 r is a potentially carcinogenic dose to the infant thyroid. While the possibility exists that the carcinogenic action may be an indirect, hormonal one, it must still be recognized that this, like leukemia, is an instance of significant car-

cinogenesis by less than 1000 rep. It seems likely that the infant thyroid is unduly susceptible, but that the adult thyroid is not...."[28]

Table II indicates the amount of ingested fission product activity to produce one rad dose to the lower large intestine and Graph 5 shows the relative doses to the gastrointestinal tract and the thyroid. It may be seen that ingestion of a given activity on the fourth and fifth days may result in nearly two and one-half times the dose to the thyroid as to the lower large intestine. For a continuous consumption of fallout material from the first hour to the 30th day the ratio of doses is about 1.7.

3. Bones

It is recognized that the intake and deposition of strontium-89 and 90 are intimately associated with the calcium in the diet. Whereas it has been assumed here that a fixed percentage of the strontium intake is deposited in the bones (reference 5). It is realized that this method involves uncertainties, as would the necessary assumptions to generalize for a wide variety of calcium—strontium ratios and intakes to cover multiple categories. In situations where doses to the bones appear to be the critical criterion (such as later times after detonation than considered here), it would be necessary to make a more precise evaluation.

Unequal distribution of isotopes in the bones has been observed. Thus, the dotted line in Graph 5 is included to suggest a possible larger dose to those regions.

Considerable data have been collected on radiation produced bone cancers. One summarizing statement that places this in proper perspective with the other factors discussed above is "... Visible changes in the skeleton have been reported only after hundreds of rep were accumulated and tumors only after 1,500 or more."[29] When one examines Graph 5 for relative doses, and reviews the data on doses versus effects to the gastrointestinal tract and possibly children's thyroids (Table IV), it would appear that exposure to the bones is not the critical factor for ingestion of fallout material under emergency conditions, for the first few weeks after detonation.

TABLE IV

Some Possible Biological Effects from Radiation Doses to Specific Organs*

Dose (Rads)	Gastrointestinal Tract	Thyroid	Bones
10,000		Minor changes in structure	
	Serious damage —survival threatened		Tumor production.
1,000	Tumor Production		
	Immediate effects such as nausea	Potential carcinogenic dose to few percent of children	Minor changes in structure
100			

* Lesser short term effects would be expected from the same doses distributed in time.

4. Summary of Biological Effects

Table IV summarizes some possible biological effects from radiation exposures. Due to inherent uncertainties in such analyses together with expected wide biological variances among individuals, Table IV is intended only to suggest a generalized picture of doses versus effects.

The physical calculations of radiation doses made above were for adults. For equal intakes of radioactivity, children probably would receive higher exposures due to the smaller organ masses, and in the case of bones a greater deposition would be expected. Also, there is the possibility of tumor production in the thyroids of some children at relatively low radiation exposures. It would appear wise therefore to establish lower limits of intake of radioactivity for children.

C. Permissible Intake

The preceding discussion attempts to give estimates of radiation doses resulting from intake of fallout material, together with some possible biological effects. How much intake is actually permitted depends upon many factors including the essentialness of the food and water to sustaining life, and one's philosophy of acceptable biological risks and damage in the face of other possible hazards such as mass evacuation. Table II and Graph 5 give estimates of the amount of contamination in food and water to produce certain radiation doses to the critical organs. Table IV indicates possible biological effects from given doses. Using these references, command decisions may be made as to permitted intake of radioactivity.

Such evaluations as attempted here are necessary and valuable for planning purposes, but once the fallout occurs the emergency of the situation may preclude immediate analysis of the food and water supplies. Further, abstaining from ingestion of food and water because it

TABLE V

Mean Body Burden of Rongelapese

Radioisotopes	Estimated Activity at One Day (μc)
Sr^{89}	1.6–22
Ba^{140}	0.34–2.7
Rare earth group	1.2
I^{131} (in thyroid)	6.4–11.2
Ru^{103}	0.013
Ca^{45}	0.019
Fissile material	0.016 (μgm)

might be contaminated could not be continued indefinitely. Therefore, the following three common sense rules are suggested:

1. Reduce the use of contaminated food and water to bare minimum until adequate monitoring can be done; use first any stored clear water and canned or covered foods; wash and scrub any contaminated foods and;

2. If the effects of lack of food and water become acute, then use whatever is available but in as limited quantities as possible. Whenever possible select what seems to be the least likely contaminated water and/or foodstuffs; and

3. Since it is especially desirable to restrict the intake of radioactivity in children, give them first preference for food and water having the lowest degree of contamination.

In an area of heavy fallout one matter to consider is the relative hazards from the external gamma exposure versus internal doses from ingestion of the material. (Inhalation is thought to contribute only relative minor doses under the conditions discussed here). The best evidence on this point is the fallout that occurred on the Rongelapese in March 1954. Those in the highest exposure group received 175 r whole-body external gamma exposure yet their body burdens of internal emitters were relatively low (Table V).[30] These and other data suggest that:

If the degree of contamination of an area is such that the external gamma exposure would permit normal and continuous occupancy after a fallout, the internal hazard would not deny it.

This is based on such reasonable assumptions of (a) about 50% reduction of gamma exposure from out-of-doors doses afforded by living a part of each day in normal family dwellings, (b) washing and/or scrubbing contaminated foods, and (c) excluding areas where relatively little fallout occurred, but into which may be transported highly contaminated food and/or water. After longer periods of time during which the gamma dose rates in an originally highly contaminated area have decreased to acceptable levels, it probably would be necessary to evaluate the residual contamination for the bone seeking radioisotopes, especially strontium-90.

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Current Problems in the Field of Respiratory Protection*

E. C. HYATT

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

THE SESSION on problems of respiratory protection is an acknowledgement by the AIHA and the ACGIH that problems do exist in this field. In August 1956, a Joint AIHA-ACGIH Ad Hoc Committee on Personal Protective Devices was appointed by these organizations. As Chairman of this Committee, I have been asked to present background information leading to the establishment of the committee. In addition, I will comment on some of the current problems recently discussed by the Joint Respirator Committee.

The main problem that has reopened discussion on these problems is the lack of approved respirators for protection against radioactive dusts. It is well known that there are no respirators approved for protection against materials significantly more toxic than lead. Back in 1950, the large scale production of the new organic phosphate insecticides focused attention on the need for respirators to protect against these highly toxic materials. A test program was initiated by the Department of Agriculture in 1951 and they have tested and recommended certain devices that are commercially available. Recognition of the hazard from beryllium in the early 40's indicated the need for respirators for a material many times more toxic than lead. However, the greatest number of workers involved are those associated with the AEC contractors working with radioactive aerosols.

Research and development work on respirators to protect against radioactive materials has largely been conducted by a few AEC contractors to solve their own problems. There has been no cooperative effort by any of the divisions in the AEC or the professional organizations to promote uniformity of respirators. Investigations in this field have been conducted by the General Electric Company at Hanford, Carbide and Carbon Company at Oak Ridge, the University of Rochester and the AEC Isotopes Division.

In 1955, the Health Division of the Los Alamos Scientific Laboratory realized that an effort must be made to establish a cooperative and uniform respiratory development project. We promoted a meeting at the Bureau of Mines in February 1956 of AEC contractors using plutonium. As a result of this meeting, the Division of Biology and Medicine of the AEC agreed to appoint a Respirator Committee from the various contractors to investigate and make recommendations in the field of respiratory protective devices. The University of Rochester is acting as Technical Advisor to the committee. To date, a representative of the University of Rochester has surveyed many of the contractors to tabulate current practices and to define the problems outlined by these contractors. At this time, the AEC Committee has not made a report. We have learned that the Chemical Corps has standardized on the use of an assault mask with a plastic hood to provide protection against plutonium aerosols.

In April 1956, a few of the current problems were called to the attention of the ACGIH Engineers Round Table and the AIHA Board of Directors. It was suggested that a committee be appointed to study the problems and make recommendations to the Associations. This Joint Committee was appointed in August of 1956.

The committee, at the start, decided to limit its activities to an investigation of the present status of respiratory protective devices in this country.

The problems enumerated by the committee fall into two broad categories. They involve the devices and the industrial hygienist and/or user. Basically, these are as follows:

1. The need for approved respiratory protective devices to protect against substances many times more toxic than lead. Examples are radioactive aerosols, beryllium, insecticides, et cetera. Therefore, the obvious need for a central government agency to investigate and compile data relative to new exposure problems, set up new approval schedules and approve all types of respiratory protective equipment.

2. Where respirators should be used, how they should be selected and how they should be used and maintained. This is understood adequately by only a small number of industrial hygienists.

The committee found that several types of

* This work was done under the auspices of the Atomic Energy Commission.

respiratory protective devices currently available are not covered by existing Bureau of Mines Approval Schedules. These are: (1) filter-type respirators for respiratory protection against particulate aerosols such as beryllium dusts and fumes, dusts impregnated with highly toxic organic phosphate insecticides (parathion), and radioactive substances; (2) paint spray respirators; (3) chemical cartridge respirators for respiratory protection against gases and vapors other than organic vapors; (4) escape-type, self-contained breathing apparatus; and (5) combination airline and self-contained breathing apparatus. Mr. Pearce advised the committee that the Bureau of Mines plans to submit the proposed performance requirements that have been developed for spray paint respirators for comment in the near future. The Bureau of Mines is actively engaged in assembling information on which to base performance requirements of respirators for respiratory protection against radioactive particulates, and hopes to resolve the problem of respiratory protection against beryllium aerosols at the same time. The Bureau of Mines also is considering action on the other types of respirators as soon as its work load permits.

The committee believes that the Bureau of Mines should be the single government agency responsible for approval. Their experience dates from 1911 when they began issuing literature on oxygen-breathing apparatus. The systematic development of modern respiratory protective equipment began in 1919. However, they must have the active support of all professional organizations involved to obtain adequate funds to carry on aggressive leadership in the development of specifications and test procedures to meet current or anticipated needs.

There is a need for the development and dissemination of more comprehensive information on respiratory protective devices and the promotion of education in the field. A comprehensive bibliography on the subject was published by Leslie Silverman in the Quarterly (Dec. 1946), covering the period from 1900 to July 1946. The Los Alamos Scientific Laboratory is completing a bibliography covering the period July 1946 through 1956. Aside from the Bureau of Mines publications, there have been six papers in the Quarterly and Archives of Industrial Hygiene since that date. However, in the last ten years Safety Engineering and National Safety News have published thirty-seven papers on respiratory protective equipment and the industrial trade journals have published twenty-three articles on the subject. All of these articles pertain to phases of selection, use and care of equipment and, in some cases, announcement of new devices. It is obvious that the safety engineers as a group have better coverage than the industrial hygienists. None of these papers, however, report on research and development in the respirator field.

Recommendations of the Joint AIHA-ACGIH Respirator Committee

The American Industrial Hygiene Association and the American Conference of Governmental Industrial Hygienists should:

1. Promote the establishment of *responsibility* in in a central agency of the federal government to investigate and compile data relative to existing and new exposure problems, set up new Approval Schedules and approve *all types* of commercially available respiratory protective equipment.
2. Promote basic research and development in the field of respiratory protective equipment.
3. Promote the development and dissemination of more comprehensive information on respiratory protective devices. These organizations should also foster an educational program covering the entire field of personal respiratory protection.
4. Assist and advise the central agency in the preparation of Approval Schedules under which the performances of respirators not covered by current schedules can be evaluated and in the revision of the requirements of current schedules. They should urge the users to present their problems to the Central Approval Agency.
5. Establish a permanent Committee on Respiratory Protective Devices to assist in implementing the program outlined.

The committee believes there are many commercially available respirators that will afford relatively good protection against many materials that are in the range of 10 to 100 times more toxic than lead. However, the state of knowledge of the industrial hygienists is such that they do not know which device to select or where to use them when they are selected. This problem was highlighted by Dr. Allen D. Brandt in his book, *Industrial Health Engineering*, published in 1947 as follows: "Respiratory Protective Devices have a distinct place in the field of industrial health engineering. That they are a last line of defense can hardly be denied. Nevertheless, where they should be used, how they should be selected and how they should be used and maintained is understood adequately by only a small number of industrial hygiene engineers."

Respirator Problems in Atomic Energy Practice

G. W. C. TAIT AND T. H. BYINGTON

Biology and Health Physics Division, Atomic Energy of Canada Limited, Chalk River, Ontario

THIS PAPER is concerned with the practice of respirator protection. Canada's Atomic Energy Project at Chalk River, as the result of the NRX reactor accident of December 12, 1952 found itself in a unique position of dependence on respirators for the protection of large crews of men engaged in dismantling and rebuilding the damaged reactor. Some of the lessons we had to learn may be of interest to those who have not had to contend with such wide-spread contamination.

At the time of the accident, Chalk River's position with respect to respiratory protection was fortunate in two respects. Most of the key men had a standard army assault respirator as a standing emergency issue. In addition, although air sampling devices were limited in number, a representative range of advanced types was available.

It was quickly evident that air contamination varied widely from place to place and over short periods of time. This made it very difficult to base control measures on individual air samples. The dislike of personnel for carrying out heavy work in respirators gave rise to pressure to remove respirators whenever a sample showing low contamination was reported. The answer to this situation was the rapid expansion of urine analysis facilities. A medical warning backed by urine analysis figures carries weight that can never be achieved by any other means.

Figure 1 shows the incidence of active urine samples at Chalk River from the occurrence of the NRX reactor accident in December 1952 until full power was again achieved in March 1954. The solid line represents the number of cases per month reported above arbitrary tolerance. It should be pointed out in passing that there is no reason for believing the maximum permissible body burden has ever been exceeded at Chalk River. The dotted line represents the percentage of all urine samples taken which were positive and corrects for changing capacity of the assay lab. A full time respirator safety Officer was appointed in June 1953. By September a programme of respirator testing and replacement by improved models was under way and by January 1954 the plant was completely equipped with improved respirators.

Figure 2 extends these curves and shows that the improvement indicated in the previous figure was not maintained. After clean up of the largest spill in atomic energy history and the introduction of what we had every reason to believe was a model respirator programme the incidence of internal contaminations increased again to a level of 30 to 50 per cent of that found under the worst conditions. The explanation of this situation requires more detailed examination. The Chalk River project as a general research and development center is a highly diversified operation in which units generally work under conditions very different from and more demanding than those postulated in the original design planning. Major areas subject to air contamination change month to month. Even at the height of the reactor decontamination this particular task did not always account for the majority of the cases of internal contamination.

Let us direct our major attention to the situation in the NRX reactor area. No one entered the reactor hall without being issued respirator protection. Nevertheless, a considerable incidence of active urine samples persisted for many months.

The upper curve (Figure 3) gives the number of positive urine samples a month among reactor workers. In this area complete control was achieved after reactor start up but this must be attributed to the removal of all important sources of contamination. The lower curve shows the average air contamination in the reactor area. One disquieting feature is the fact that internal contaminations do not fall off directly with control of air contamination. It is not possible to attribute this entirely to the retention curve for human internal contamination.

Careful examination of a wide range of commercial and military respirators under difficult working conditions revealed a host of possible causes for these discrepancies. Leakage around the facepiece due to poor fit was common. Oro-

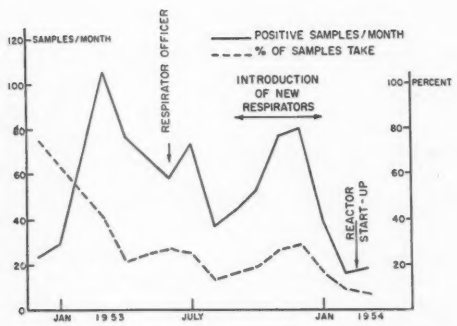

FIGURE 1. Incidence of active urine samples at Chalk River while the NRX reactor was undergoing repair.

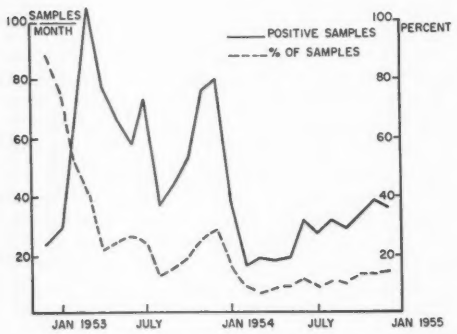

FIGURE 2. Active urine samples over an extended period.

nasal types (half masks) were particularly susceptible to poor fit leaving a gap over the bridge of the nose. Cases were found where internal supporting webbing had been cut to improve the comfort. Constructional flaws gave leaks around poorly sealed eyepieces and due to burrs in valve seats. Faulty decontamination sometimes left a hair or thread preventing proper seating of a valve. Some cases were found where the valve action had been "improved" by insertion of a paper clip to ease breathing. Impatience with difficulties in giving orders in noisy areas often resulted in supervisory personnel raising the facepiece or even wearing the respirator on top of the head like a hat.

Paper filters were often improperly centered in the container, permitting leakage. In addition, rough usage often tore the paper at the rim or at center supports. Unexpected sources of major internal contamination were discovered, for example when men received more internal contamination from dust raised in removing work clothes in the change room than they did when working on the reactor itself.

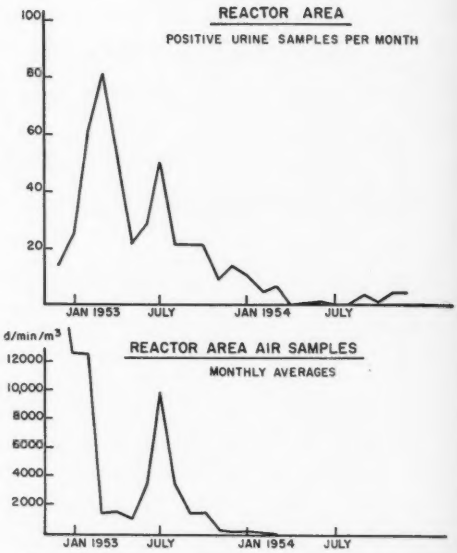

FIGURE 3. Upper graph: active urine samples among reactor workers. Lower graph: average air contamination in the reactor area.

These various sources of breathing hazard were tackled in a variety of ways.

A respirator safety officer was made completely responsible for respiratory protection as it was apparent that only a person giving his total attention could hope to cope with the host of problems. His first point of attack was to give instruction in proper fitting and usage. A gas test chamber proved valuable. In order to encourage a proper attitude to respirator care, the issue, checking and decontamination of respirators was systematized so that each individual knew his responsibilities. Because of the popularity of the oro-nasal or half face respirator, considerable effort was applied to removing its defects. A promising industrial type was chosen and modified as in Figure 4. A web head harness was substituted for the single band to overcome the tendency for poor fit at the bridge of the nose. A military type, cemented, pleated paper filter canister was substituted for the rather vulnerable original bellows type filter.

Difficulties of speech transmission were met by issue of a number of army type respirators with special speech diaphragms. In addition more careful planning of work procedures cut down the need for discussions at the active site.

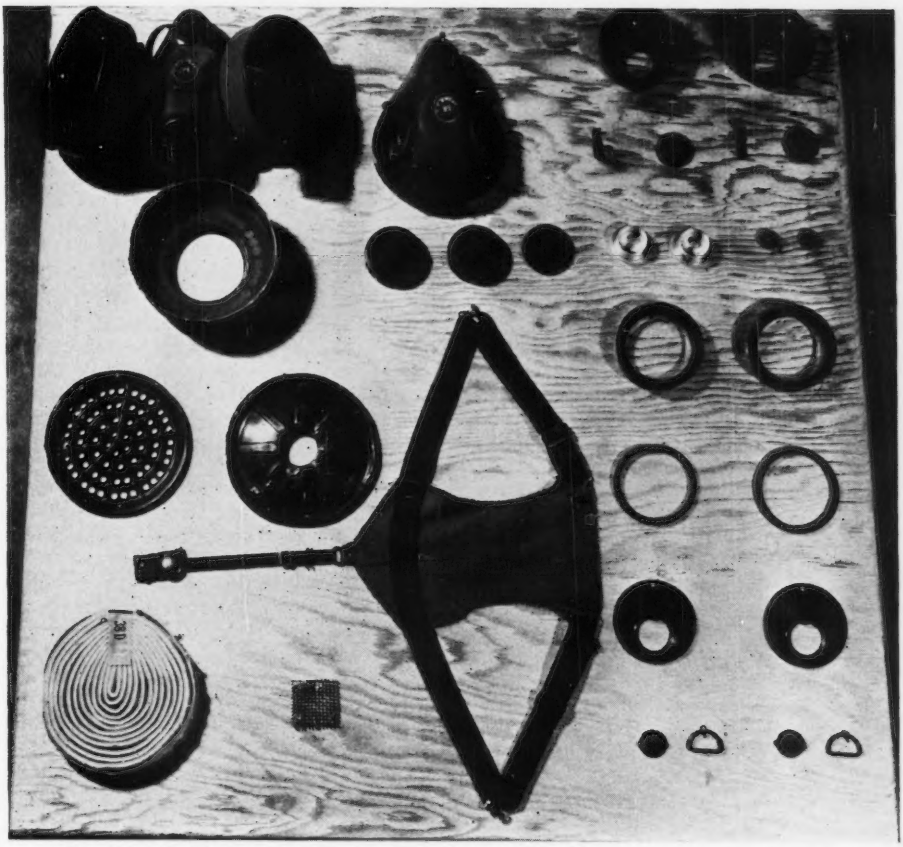

FIGURE 4. Modified oro-nasal respirator: upper left, complete unit; center, web type head harness; lower left, pleated filter; upper right, adaptors to permit use of military standard canisters on an industrial mask.

Contamination while undressing was controlled by providing special dressers to assist after the more active tasks.

As indicated in Figure 2 our experience has been that work in heavily contaminated areas will continue to give some incidence of internal contamination despite the most careful respirator programme. A reduction to half to one fifth is the most that can be expected. This in part is due to inevitable human failures and in part to the fact that the very small quantities of radioactive matter involved in internal contamination can achieve entry by other routes than through the intact respirator.

Nevertheless these considerations must strengthen rather than weaken the case for a sound respirator programme. Only if we have confidence in the reliability of this protection can we seek out and find the other more obscure sources of internal contamination.

A Discussion of the Bureau of Mines Approval Schedules for Respiratory Protective Devices

S. J. PEARCE

Chief, Respirator Section, Branch of Health Research, Division of Health, Bureau of Mines, U. S. Department of the Interior, Pittsburgh, Pennsylvania

THE PURPOSE of this paper is to explain briefly the operation of the Bureau of Mines approval system for respiratory protective devices, to discuss certain considerations in regard to the performance of respirators, and to outline this Bureau's present activities and proposed plans in regard to broadening its respirator approval system.

The Bureau of Mines has prepared a series of schedules setting forth the minimum requirements that various types of equipment should meet to be considered safe and satisfactory for use in certain hazardous and unhealthful conditions. These schedules cover a wide variety of devices, ranging from explosives to electrically operated mine locomotives. Only those Bureau of Mines schedules under which respiratory protective devices are tested and approved will be discussed.

The Bureau of Mines has five approval schedules[1] under which it tests and approves the following types of respiratory protective devices: Self-contained breathing apparatus, gas masks, supplied-air respirators, nonemergency gas respirators (chemical cartridge respirators), and dust, fume, and mist respirators. The approval testing work of the Bureau of Mines is done at its Central Experiment Station, Pittsburgh, Pa.

Application for approval testing of these devices under the Bureau's schedules is voluntary on the part of the respirator manufacturers. The Bureau of Mines has no regulatory power to demand that all respiratory protective devices sold in this country be approved. Rather, it serves as an impartial testing agency whose approval indicates to prospective users that the device has met certain performance requirements. The relative merits of approved respirators of the same type cannot be commented upon by the Bureau.

The schedules set forth minimum performance requirements that respiratory protective devices must meet to be approved. These performance requirements are designed to assure that the devices will provide adequate protection for a suitable period, will be reasonably comfortable and convenient to wear, and will be constructed, in all of their parts, of materials suitable for the purpose they must serve. Performance requirements rather than design specifications allow the manufacturers wide latitude in their choice of materials and design.

For the sake of brevity, the word "respirator" will be used to refer to respiratory protective devices in general, and the specific names of the various types of respirators will be given only when reference is made to them.

A Bureau of Mines schedule for a certain type of respirator is prepared in the following manner: The field of use of the respirator is reviewed, and those characteristics that the respirator should have are considered from both the idealistic and the practical standpoints. Tentative performance requirements are set up, test apparatus and procedures are devised, and tests are made on respirators of this type that are currently available. On the basis of these tests, such modifications of the requirements as seem desirable are made. An effort is made to anticipate possible future developments and modifications of that type of respirator and its field of use and to make the schedule flexible enough to be applicable over as wide a range of design as possible. A tentative draft of the proposed schedule is sent for comment and criticism to industrial hygienists and safety engineers known to be well qualified to comment on it, as well as to the manufacturers and prospective users of

[1] Bureau of Mines, Respiratory Protective Apparatus—Tests for Permissibility; Fees: Sched. 13D, Self-Contained Breathing Apparatus, Sept. 22, 1956 (Code of Federal Regulations reference: 30 CFR Part 11); Sched. 14F, Gas Masks, Apr. 23, 1955 (Code of Federal Regulations reference: 30 CFR Part 13); Sched. 19B, Supplied-Air Respirators, Apr. 19, 1955 (Code of Federal Regulations reference: 30 CFR Part 12); Sched. 21A, Filter-Type Dust, Fume, and Mist Respirators, Apr. 19, 1955 (Code of Federal Regulations reference: 30 CFR Part 14); and Sched. 23A, Nonemergency Gas Respirators (Chemical Cartridge Respirators), Apr. 23, 1955 (Code of Federal Regulations reference: 30 CFR Part 14a).

the respirator. Comments and criticisms are weighed, and acceptable changes based upon this advice are made in the proposed schedule. All the suggested changes may not be incorporated in the schedule; but the reasons why they are not to be incorporated are transmitted to those who suggested the changes, and further argument for the changes is allowed. If the extent of the changes in the second draft of the schedule warrant it, further comment and criticism are invited. The final draft of the schedule is published in the Federal Register as a Notice of Proposed Rule Making. The public is given 30 days to submit written data, views, or arguments in regard to the proposed schedule to the Director of the Bureau of Mines. All relevant material received during this period is considered before final publication of the schedule in the Federal Register.

Before formal submission of a respirator for Bureau of Mines approval, the manufacturer may visit or communicate with this Bureau at Pittsburgh to obtain criticisms of proposed designs of the respirator or to discuss test requirements. No charge is made for this consultation, and no written report is made to the manufacturer. The Bureau does no development work, as such, on respirators, but in the course of the consultation mentioned above and during the formal approval testing, many suggestions have been made to, and accepted by, respirator manufacturers as to how their respirators might be improved as regards safety, comfort and convenience, and durability.

Before a respirator may be tested for approval by the Bureau of Mines, the manufacturer must fulfill certain pretest requirements. He must file an application that contains (1) a description and complete drawings of the respirator, (2) a statement that the device is completely developed and is of the design and materials believed suitable for a finished marketable product, (3) a statement that the device has been tested according to the requirements of the pertinent schedule and has met them, (4) a statement regarding the nature, adequacy, and continuity of the control of the quality of the respirator, (5) a request that the necessary inspections and tests leading to approval be made, and (6) a fee to cover the cost of the tests.

Upon receipt of the manufacturer's application the Bureau proceeds with the inspections and tests, comparing the data obtained with those submitted by the manufacturer. If the results of the inspection and tests are satisfactory and the drawings and description of the device are in order, the Bureau prepares appropriate approval plates which are transmitted to the manufacturer with a letter stating that the respirator has been approved by the Bureau of Mines.

If the respirator fails to meet the schedule requirements, the Bureau attempts to determine the cause of the failure and makes suggestions to the manufacturer as to how the difficulty might be overcome. After the manufacturer has made appropriate changes in the respirator and has tested the revised respirator, he resubmits it to the Bureau with a fee proportional to the additional tests required.

The approval label gives the limitations of the approval, such as the maximum concentration of gas in which a gas mask may be worn, lists the approval markings on the parts that make up the approved respirator, and states special precautions that must be observed in using the respirator. If a respirator is not used properly or if it is used in conditions other than those covered by the approval label, the approval of that individual respirator is invalidated.

Bureau of Mines approval on a respirator obligates the manufacturer to make his respirator according to drawings, designs, and specimens that he submitted to the Bureau and that were considered and included in the approval. Any changes whatsoever a manufacturer may desire to make in a respirator after approval must be submitted to and accepted by the Bureau before they are adopted.

Bureau of Mines approval applies only to the respirator as a unit and not to its component parts. For instance, suppose that approvals had been granted to four respirator manufacturers, A, B, C, and D, on four entirely different universal-type gas masks. An assembly of A's canister harness, B's canister, C's timer, and D's facepiece would not constitute an approved assembly, even though these individual items are parts of approved gas masks. This approval of complete devices applies throughout the entire Bureau of Mines approval system and is not peculiar to schedules that deal with respiratory protective equipment.

The following discussion is based on questions that have been brought up in regard to some of the requirements of the approval schedules.

Comfort is a relative and subjective term, one definition of which is "freedom from pain, or trouble." It is, perhaps, a poor word to use in connection with a respirator, aside from the respiratory protection that is afforded the wearer from irritant or harmful gaseous or particulate contaminants in the surrounding atmosphere. There is not at present, nor will there be in

the future, a respirator that will make the wearer's face and head more comfortable when the respirator is worn in respirable air than when it is not worn. In order to fit a full- or half-mask facepiece in a gas- or dust-tight manner to a person's face, it is necessary to apply tension to the head harness straps or head bands. The amount of tension that must be applied depends on the shape and fleshiness of the wearer's face and on the degree of protection desired. A person with a full, round face usually needs to apply only moderate tension to full facepiece head harness straps to keep the facepiece in place and to obtain a gastight fit. He can wear the facepiece for a prolonged period in reasonable comfort. On the other hand, a person with a long, thin face, having high cheek bones, might have to apply extreme tension to the head harness to obtain the same degree of protection using the same facepiece, and he might complain, with cause, that the facepiece was very uncomfortable to wear. In fitting and wearing identical half-mask facepieces, some persons must, because of the shape and size of their faces, apply more tension than others to the headbands, with a corresponding increase in discomfort. There is considerable room for improvement of both types of facepieces in regard to the "comfort" afforded wearers having widely different facial shapes and sizes.

The tightness of fit of facepieces designed for protection against gases, vapors, and metal fumes is tested by having 15 to 20 persons with widely varying facial shapes and sizes wear the complete respirator in a test atmosphere that will warn the wearer if an undue amount of it enters the facepiece. The air in the test space may contain 100 p.p.m. of isoamyl acetate, 1 per cent of ammonia, or 2 per cent of phosgene, depending on the facepiece being tested. Isoamyl acetate, in the above concentration, and 1 per cent ammonia give comparable results. That is, if the facepiece allows enough isoamyl acetate to leak into the breathing zone of the wearer to be faintly detectable by its odor, the wearer would be able to detect a faint odor of ammonia if he entered a 1 per cent ammonia-air mixture with an appropriate canister.

A facepiece that has been adjusted to the wearer so that he can wear it in either 100 p.p.m. of isoamyl acetate or 1 per cent of ammonia without detecting the odor of these test materials could still allow enough leakage of phosgene, when worn in 2 per cent of this gas, to cause the wearer to leave the test space hurriedly. The odor of ammonia can be detected faintly when 50 p.p.m. is present, whereas the odor of phosgene can be detected readily when 1 p.p.m. is present. Thus, facepieces worn under the same conditions in 1 per cent (10,000 p.p.m.) of ammonia or 2 per cent (20,000 p.p.m.) of phosgene that would leak enough to allow ammonia or phosgene to be detected definitely by the wearer by odor would have efficiencies of 99.5 and 99.995 per cent, respectively.

There is a widespread notion that eyeglasses or spectacles with metal temple pieces extending over and back of the ears can be worn with safety with gas-mask facepieces, especially if the temple pieces are flat and lie close to the wearer's temples. Tests at the Bureau of Mines in a 1 per cent ammonia-air mixture have shown that none of the commercially available full facepieces can be worn with such spectacles without the wearer detecting a definite to strong odor of ammonia. When persons had thin faces and high cheek bones, the leakage of ammonia was enough to drive them out of the test atmosphere. It would be impossible for anyone to stay in a 2-per cent phosgene-air mixture with such an assembly. Anyone who believes differently is invited to visit the Bureau's Respirator Laboratory in Pittsburgh for a personal demonstration.

The term "efficiency," as applied to filters for particulate matter, is meaningless unless the conditions under which efficiency is measured are strictly defined. To employ an example that has been used a number of times, "Chicken wire is 100 per cent efficient against chickens, but not against sparrows." Hence, among other things, one should specify the size characteristics of the test aerosol. As the particulate matter is removed by the filter, plugging of the interstices of the filter occurs, and its efficiency increases. When a filter is tested against an aerosol in which the concentration of particulate matter is high enough to cause significant plugging of the filter, the efficiency changes from minute to minute. If the average efficiency is determined over a protracted period, this value would depend on the concentration of particulate matter and the rate at which it was drawn to the filter.

The ability of a filter or a gas-mask canister to remove particulate matter or gases, respectively, is not the final criterion of the protection afforded by a dust respirator or a gas mask. A dust respirator having a perfect filter would be a dangerous and worthless device for protection against highly toxic dispersoids if the facepiece were not, or could not be, adjusted to a dust-tight fit on the wearer, or if the exhalation valve or the seal between the filter and the filter holder allowed dust to enter the facepiece. Conversely, the combination of a perfect facepiece and a poor filter would be just as bad. A res-

pirator will not afford more protection than its least effective component.

The limit set for the maximum resistance allowed for an approved respirator is a compromise between the desire for very low resistance and the desire to keep the respirator's bulk to a minimum. Certainly, respirators could be built that would have very low inhalation resistances, but this would necessitate using filters with much larger filter areas than are used on current respirators, with corresponding increases in overall size of the respirators. Respirators for protection against metal fumes need dense filters to remove the very fine fume particles from the air drawn to them. If initial inhalation resistance only were to be considered, the filter area would not need to be very large; but, since resistance increases with fume load on the filter, the filter area must be relatively large to keep the final resistance within limits. Practical limitations on the size of gas-mask canisters also have been considered in setting the maximum inhalation resistance for gas masks.

Several types of respirators are currently available that are not covered by existing Bureau of Mines approval schedules. These are: (1) Filter-type respirators for protection against particulate aerosols, such as beryllium dusts and fumes, dusts impregnated with organic phosphorus insecticides (parathion), and radioactive substances; (2) paint-spray respirators; (3) chemical cartridge respirators for respiratory protection against gases and vapors other than organic vapors; (4) escape-type self-contained breathing apparatus; and (5) combination air-line and self-contained breathing apparatus.

The Bureau of Mines has been working for some time to develop test procedures and requirements for paint-spray respirators. A preliminary draft describing these procedures and requirements has been sent to a limited group for comment before a more complete draft is prepared for wider distribution.

The Bureau of Mines is seriously considering the feasibility of establishing performance requirements for chemical-cartridge respirators for gases and vapors other than organic vapors, for escape-type self-contained breathing apparatus, and for combination air-line and self-contained breathing apparatus. Work is also in progress on a revision of the performance requirements for supplied-air respirators.

Several groups and individuals have urged the Bureau of Mines to prepare performance requirements for respirators designed for respiratory protection against radioactive particulate matter. At present, this Bureau is actively engaged in assembling information on which to base these performance requirements. To this end, and to expedite matters, the Bureau of Mines is forming a small committee to cooperate closely with it to work out details of performance requirements and test procedures for such respirators, to assure that respirators approved under these requirements and by these test procedures would be safe and suitable for their intended field of use. Consideration also will be given to the broad field of respiratory protection against radioactive substances. The committee is composed of individuals chosen because of their interest in the field of respiratory protection and their specialized knowledge of: (1) The hazards associated with the use of radioactive substances, (2) industrial hygiene and industrial medicine, (3) unclassified developments in respiratory protection for the armed forces, (4) problems associated with the development and production of respirators, and (5) the approval testing of respirators. The results of the work of this committee will be disseminated widely for comment before final criteria are established.

This cooperative effort is one instance of a procedure that could aid materially in solving respiratory-protection problems arising from new technologic developments, namely, close liaison between the Federal Bureau of Mines and the manufacturers and users of respirators. The users or prospective users of respirators should acquaint respirator manufacturers and the Bureau of Mines with their respiratory-protection problems, so that the manufacturers can develop respirators designed to meet these problems and so that the Bureau of Mines can formulate approval schedules under which the performances of these respirators can be evaluated. The increasing complexity of respiratory-protection problems makes such cooperation almost mandatory.

A Comparison of Performance Standards and Tests Specified by Bureau of Mines Schedule 14F and by the Chemical Corps for the M9A1 Mask

GERALD J. FLEMING

Protective Development Division, U. S. Army Chemical Warfare Laboratories

I. Object

THE OBJECT of this presentation is to provide a comparison of the test methods and performance standards prescribed by Bureau of Mines under Schedule 14F with the corresponding test methods and performance standards used by the Chemical Corps for the M9A1 mask under pertinent purchase specifications.

II. Introductory Remarks

In order to better understand the subject matter, I would first like to offer a few remarks about the design and construction of the gas mask as typified by the Chemical Corps' present standard mask. This is the M9A1 Field Protective Mask, and a schematic diagram, illustrating its construction and method of operation is demonstrated on the attached Figure 1. Basically, this mask consists of a facepiece and canister. The facepiece itself is composed of several component parts which include the nosecup, eyelenses, outlet valve, and headharness. The canister is basically an aluminum shell containing a pleated aerosol filter element and a layer of charcoal. The mask operates as follows: The contaminated air is drawn through the canister during the inhalation cycle of the wearer's breathing. The filter element removes any particulate matter, either solid or liquid, and the charcoal layer removes any gaseous contaminants. The air after passing through the canister is routed through a built-in Tissot tube to the underside of the eyelenses. After passing over the eyelenses, the air is inspired into the nosecup and breathed by the wearer. Upon exhalation, the expired air passes out of the gas mask through the outlet valve.

Also in the way of introductory remarks I would like to present certain information as to the objectives of the Bureau of Mines' work as compared to that of the Chemical Corps, in the field of gas masks and testing thereof. Bureau of Mines is responsible for promotion of the use of safe, satisfactory and reliable respiratory devices for protection of personnel against industrial-type atmospheric contaminants. To insure that such devices will be available, the Bureau has established schedules which give minimum performance standards for various classes and types of respiratory protective devices and makes available to the public at intervals, a listing of the devices which have been approved. Thus manufacturers desiring to obtain Bureau of Mines' approval for their masks, submit same to the Bureau for their compliance with these minimum performance standards. The submission of masks for approval is entirely voluntary on the part of the manufacturer, since the Bureau of Mines has no regulatory powers requiring such submission. The wide acceptance of the Bureau of Mines' approval encourages manufacturers to submit their devices for approval. With regard to the Chemical Corps, this service is responsible for research, development, procurement, storage, issue and maintenance of masks for use by the military forces. The M9A1 mask is the result of years of research and development effort involving extensive engineering and user acceptability testing. In order to procure the developed item in the large quantities which the Department of Defense requires, the item is translated into elaborate and detailed procurement documents, such as specifications and drawings. The drawings are used as the basis for insuring that the purchased item will be identical in design and construction to the developed item. The specifications contain minimum performance standards and corresponding test methods designed to insure that the purchased mask is equal in performance to the developed item. Thus, in making the comparison between the Bureau of Mines and the Chemical Corps testing methods, I propose to provide a comparison between the minimum performance standards and test methods as established by the Bureau of Mines Schedule 14F with respective standards and test methods prescribed by the

Chemical Corps in their purchase specifications. Further, I shall provide some information relative to the type of engineering and user tests conducted on the M9A1 mask during and subsequent to its development to insure its suitability for the intended purpose.

III. Comparison

In making the comparison between the Bureau of Mines and Chemical Corps performance standards and test methods, I have presented such information in seven tables. In tables I, II and II-A, there is presented a comparison of the performance standards and test methods for canisters. In tables III and IV, there is presented a comparison of the performance standards and tests on the facepiece and other components. In table V, there is presented information on the performance standards and tests for the complete gas mask as given in Bureau of Mines Schedule 14F. There is no comparative information for the Chemical Corps complete mask, since such testing is not called for. With reference to the comparative information on canisters, as given in tables I, II and II-A, it will be noted that there are three main criteria established for evaluating the efficiency of the canister. These are: (1) gas life, (2) particulate penetration, and (3) air resistance. With reference to gas-life testing, it can be seen that there is some general similarity in the test methods employed although the test gases and the conditions of test differ in many respects. With regard to the particulate penetration tests, there is little similarity in the tests prescribed. The Bureau of Mines schedule calls for tests against tobacco smoke and diphenylaminechlorarsine (DM) smoke. Two different kinds of approval are awarded by the Bureau of Mines, depending on whether the canister passes the tobacco smoke test and/or the DM smoke test. The first type of approval, based on passing the tobacco smoke requirement, covers masks "with filters that afford respiratory protection against smokes from ordinary fires and limited respiratory protection against dusts, fumes, mists and fogs but do not afford respiratory protection against toxic smokes of warfare." The second type of approval, based on passing the DM test, covers masks "with filters that afford respiratory protection against toxic dusts, fumes, mists, fogs and smokes." The tobacco smoke and DM tests as used by the Bureau of Mines are solid particulate tests. Conversely, the Chemical Corps test requirement and test method for efficiency of aerosol particulate removal is based on the so-called dioctyl phthalate (DOP) test. In this

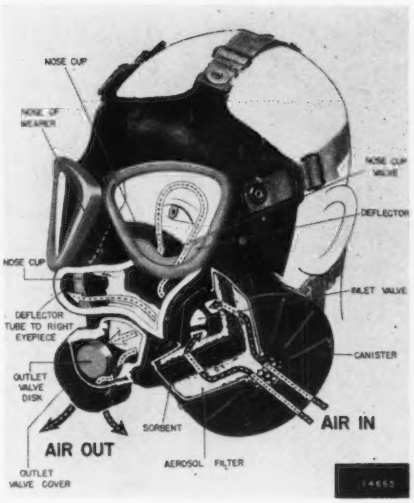

FIGURE 1

test, dioctyl phthalate is generated as a particle of approximately three-tenth micron in diameter, and is a homogeneous liquid aerosol. This DOP test has been found to be much more stringent than the solid particulate test and it is generally held that filters showing adequate liquid aerosol protection demonstrate adequate solid aerosol protection, but the converse is not necessarily true. It is also generally held that a much superior filter is required to pass the dioctyl phthalate than is required to pass the solid particulate test.

Inhalation air resistance requirements, as run on canisters by Bureau of Mines and Chemical Corps, are essentially equivalent. In the data presented in tables III and IV, which compare the performance standards and tests for the facepiece and other components, it will be noted that the Burean of Mines specifies general rather than detailed tests and performance requirements as it does in the case of canisters. On the other hand, the Chemical Corps specifications for facepieces and other components require detailed testing to insure their compliance with the prescribed standards.

For testing the complete mask, as shown in table V, the Bureau of Mines calls for extensive man tests, generally in an atmosphere of the test gas to evaluate the performance of the complete mask. The man tests also involve a schedule of activity of the wearer to insure that the masks will provide satisfactory protection under actual use conditions. No corresponding tests, such as these, are prescribed by the Chemical

TABLE I

Performance Standards and Tests for Canisters as given in Bureau of Mines Schedule 14F

Canister referenced in Bureau of Mines Schedule 14F	Test gas	Gas test requirements: Low concentrations and low flow rate tests — Bureau Mines Schedule 14F[A] & [G] — Influent concentration			Maximum effluent. conc. allowed			Minimum life	Gas test requirements: High concentrations and high flow rate tests — Bureau Mines Schedule 14F[B] — Influent concentration			Maximum effluent conc. allowed			Minimum life	Particulate test requirement — Bureau Mines Schedule 14F	Inhalation air resistance requirement — Bureau Mines Schedule 14F[C]
		%	ppm	mg/l	%	ppm	mg/l	min	%	ppm	mg/l	%	ppm	mg/l	min		mm H_2O
Type A Acid Gas Canister	Chlorine (Cl_2)[G]	0.50	5,000	14.50	0.0005	5	0.0145	88	3.00	30,000	87.00	0.0005	5	0.0145	11		
	Hydrogen Cyanide (HCN)	0.50	5,000	5.50	0.0005	5	0.0055	88	2.00	20,000	22.00	0.0005	5	0.0055	11		76.2
	Sulphur Dioxide (SO_2)	0.50	5,000	19.65	0.0005	5	0.01965	88	2.00	20,000	78.60	0.0005	5	0.01965	11		(maximum)
	Phosgene ($COCl_2$)	No test specified							2.00	20,000	81.00	0.0005	5	0.0202	11		
Type B Organic Gas Canister	Carbon Tetrachloride (CCl_4)[G]	0.50	5,000	31.50	0.0005	5	0.0315	96	2.0	20,000	126.00	0.0005	5	0.0315	12		76.2 (maximum)
Type C Ammonia Gas Canister	Ammonia (NH_3)[G]	2.00	20,000	13.9	0.01	100	0.007	36	3.00	30,000	20.85	0.010	100	0.007	12	*Original Test*[E] 50% Efficiency (minimum) when tested vs tobacco smoke	76.2 (maximum)
Type D Carbon Monoxide Canister (for regular service)	Carbon Monoxide	1.0	10,000	11.45	0.0036	36	0.040	240	2.0	20,000	22.8	0.1000	1000	1.145	15	*Added Test (1942)*[F] Allowable leakage is 0.13 mmg per liter of DM smoke	76.2 (maximum)
		0.5	5,000	5.73	0.0036	36	0.040	60									
Type N Universal Gas Canister	Chlorine (Cl_2)	0.50	5,000	14.50	0.0005	5	0.0145	44	2.00	20,000	56.00	0.0005	5	0.0145	5.5		
	Hydrogen Cyanide (HCN)	0.50	5,000	5.50	0.0005	5	0.0055	44	2.00	20,000	22.00	0.0005	5	0.0055	5.5		
	Sulphur Dioxide (SO_2)	0.50	5,000	19.65	0.0005	5	0.01965	44	2.00	20,000	78.60	0.0005	5	0.01965	5.5		
	CarbonTetrachloride (CCl_4)	0.50	5,000	31.50	0.0005	5	0.0315	48	2.00	20,000	126.00	0.0005	5	0.0315	6		82.5
	Ammonia (NH_3)	2.00	20,000	13.90	0.0100	100	0.007	48	3.00	30,000	20.85	0.0100	100	0.0070	6		(maximum)
	Carbon Monoxide (CO)	1.00	10,000	11.45	0.0036	36	0.040	240	2.00	20,000	22.80	0.1000	1000	1.145	15		
	Carbon Monoxide (CO)[D]	0.50	5,000	5.73	0.0036	36	0.040	60	No test specified								
	Phosgene ($COCl_2$)	No test specified							2.00	20,000	81.00	0.0005	5	0.0202	5.5		

[A] *Test Conditions (ref. Bureau Mines Schedule 14F).*

	Phosgene ($COCl_2$)	No test specified	2.00	20,000	81.00	0.0005	5	0.0202	5.5		

[A] *Test Conditions* (*ref. Bureau Mines Schedule 14F*).
Relative humidity of test atmosphere—50 ± 5%.
Temperature of test—room (about 25°C.).
Rate of flow of test atmosphere—32 l./min. continuous flow.

[B] *Test Conditions* (*ref. Bureau Mines Schedule 14F*).
Relative humidity of test atmosphere—50 ± 5%.
Temperature of test-room (about 25°C.).
Rate of flow of test atmosphere—64 l./min. continuous flow.

[C] *Air Resistance* tests made with air flowing at a rate of 85 liters. (3 cfm) per minute (ref. Bureau Mines Schedule 14F).

[D] This test is made to determine the activity of the catalyst which effects the oxidation of the CO to CO_2, under the adverse condition of a low temperature. The canister and a precooling coil for the entering test atmosphere are immersed in an ice-water bath. The relative humidity of the test atmosphere is 100% at 0°C.

[E] *Test Conditions* (*ref. Bureau Mines Technical Paper 394, 1926*)
Rate of flow of test atmosphere—85 l./min. continuous flow.
Test agent—specially prepared tobacco smoke.
Efficiency determined during first 5 minutes of test.

[F] *Test Conditions* (*ref. Cml C Pamphlet No. 2, Part 1, Section C-DM and letter Acting Chief, Health Branch, Bureau of Mines, 31 January 1951, to Chief, Protective Division, Army Chemical Center, Md.*).
Rate of flow of test atmosphere—32 l./min. continuous flow.
Test agent—solid DM (Diphenylaminechlorarsine).
Temperature of test—room (about 25°C.).
Machine test period—5 minutes.
Concentration of DM in test atmosphere—50 mg./l.

[G] To meet the chemical stability requirements the gas life of the respective canister shall be at least one-half the minimum life requirement of the gas indicated when tested after equilibration under the following conditions.
a. *Dry Conditions.*
Relative humidity of air—25%.
Temperature of test—room (about 25°C.).
Rate of flow of air—64 l./min. continuous flow.
Time—6 hours.
b. *Moist Conditions*
Relative humidity of air—85%.
Temperature of test—room (about 25°C.).
Rate of flow of air—64 l./min. continuous flow.
Time—6 hours.

TABLE II

Performance Standards and Tests for Complete M11 Canister and Component Parts as given in Chemical Corps Specifications

M11 Canister Component Part or Complete M11 Canister	Gas Test Requirement				Particulate Test Requirement	Air Resistance Requirement	Other Pertinent Tests	
	Test Gas	Pertinent Chemical Corps Specification			Pertinent Cml C Spec.	Pertinent Cml C Spec.	Test	Requirement
		Influent Concentration						
		%	ppm	mg./l		mm H_2O		
C6 Filter Paper (Specification MIL-F-13785A, 30 November 1955)	Not applicable	Not applicable			Penetration shall not exceed 0.05% DOP[F]	44[I] (maximum)	Tensile strength	2.0 lb./inch width
							Water repellency	20 inches H_2O (minimum)
							Mildew resistance	no growth
Aerosol Filter Element (made from C6 Filter Paper) (Specification MIL-F-10969A, 2 November 1955)	Not applicable	Not applicable			Penetration shall not exceed 0.015% DOP[G]	10[J] (maximum)	None	
Whetlerized Charcoal (Specification MIL-C-13724 (Cml C), 22 October 1954	Chloropicrin (CCl_3NO_2)[A]	0.68	6800	50	Not applicable		Hardness	80 (minimum)
	Hydrocyanic Acid (HCN)[B]	0.83	8300	10			Bulk density	0.57 gm./ml. (maximum)
	Phosgene ($COCl_2$)[C]	0.45	4500	20			Moisture content	2.0% (maximum)
	Cyanogen Chloride (CNCl)[D]	0.145	1450	4			Particle size	Nominal size 12-30 sieve
	Arsine (AsH_3)[E]	0.29	2900	10				
Complete Mll Canister (Specification 197-54-597, 20 January 1955)	Chloropicrin (CCl_3NO_2)[A]	0.68	6800	50	Penetration shall not exceed 0.025% DOP before and after rough handling[H]	75[K] (maximum) 50 (minimum)	Canister air leakage	At 5.5 psi, shall not leak in excess of 5 ml./min.

I. *Gas Tests*

[A] *Test Conditions (Reference: Cml C Pamphlet No. 2, Part I, Section A)*
Relative humidity of test atmosphere—50%.
Temperature of test—room (about 25°C.).
Rate of flow of test atmosphere—32 l./min. continuous flow.
Moisture content of charcoal—2% maximum.
Rough handling—10 minutes on E4 Rough Handling Machine.

[B] *Test Conditions (Reference: Cml C Pamphlet No. 2, Part I, Section I).*
Relative humidity of test atmosphere—50%.
Temperature of test—room (about 25°C.).
Rate of flow of test atmosphere—32 l./min. continuous flow.
Moisture content of charcoal—2% maximum.

[C] *Test Conditions (Reference: Cml C Pamphlet No. 2, Part I, Section B).*
Relative humidity of test atmosphere—50%.
Temperature of test—room (about 25°C.).
Rate of flow of test atmosphere—32 l./min. continuous flow.
Moisture content of charcoal—2% maximum.

D *Test Conditions (Reference: Cml C Pamphlet No. 2, Part I, Section N).*
Relative humdity of test atmosphere—80%.
Temperature of test—room (about 25°C.).
Rate of flow of test atmosphere—50 l./min. intermittent flow.
Moisture content of charcoal—humidified at 80% R.H.

E *Test Conditions (Reference: Cml C Pamphlet No. 2, Part I, Section N).*
Relative humidity of test atmosphere—80%.
Temperature of test—room (about 25°C.).
Rate of flow of test atmosphere—50 l./min. intermittent flow.
Moisture content of charcoal—humidified at 80% R.H.

II. *Dioctyl phthalate (DOP) Liquid Aerosol Tests.*

F *Test Conditions (Reference: Cml C Directive 334).*
Sample area—100 sq. cm.
Air flow—32 l./min. continuous flow.
Influent DOP concentration—133 mmg./l.
Rough handling—10 minutes on E4 Rough Handling Machine.

G *Test Conditions (Reference: Method 102.8 of Specification MIL-F-10462).*
Sample area—500–600 sq. cm.
Air flow—32 l./min. continuous flow.
Influent DOP concentration—133 mmg./l.

H *Test Conditions (Reference: Method 502.1 of Specification MIL-F-10462).*
Sample area—500 to 600 sq. cm.
Air flow—32 l./min. continuous flow.
Influent DOP concentration—133 mmg./l.

III. *Air Resistance Tests.*

I *Test Conditions (Reference: Cml C Directive 334).*
Sample area—100 sq. cm.
Air flow—32 l./min. continuous flow.

J *Test Conditions (Reference: Cml C Directive 593).*
Sample area—500 to 600 sq. cm.
Air flow—32 l./min. continuous flow.

K *Test Conditions (Reference: Cml C Directive 112).*
Sample area—500 to 600 sq. cm.
Air flow—85 l./min. continuous flow.

TABLE II-A

Summary Comparison of Pertinent Tests for Canisters as Given in Bureau of Mines Schedule 14F and Applicable Chemical Corps Specifications

Test Conditions	As Given in Bureau Mines Schedule 14F	As Given in Applicable Chemical Corps Specifications
A. *Gas Tests*		
Test Gas and Concentration of Test Gases	1. Chlorine (Cl_2)—0.5% and 3.0% 2. Hydrogen Cyanide (HCN)—0.5% and 2.0% 3. Sulfur Dioxide (SO_2)—0.5% and 2.0% 4. Phosgene ($COCl_2$)—0.5% and 2.0% 5. Carbon Tetrachloride (CCl_4)—0.5% and 2.0% 6. Ammonia (NH_3)—2.0% and 3.0% 7. Carbon Monoxide (CO)—0.5%, 1.0% and 2.0%	1. Chloropicrin (CCl_3NO_2)—0.7% 2. Hydrogen Cyanide (HCN)—0.8% 3. Phosgene ($COCl_2$)—0.5% 4. Cyanogen Chloride (CNCl)—0.15% 5. Arsine (AsH_3)—0.3% *NOTE*: Above gases tested on charcoal; only chloropicrin tests on completed canister
Concentration of Test Gases; Flow Rate and Relative Humidity of Test Atmosphere	1. *At Low Concentration and Low Flow Rates* a. 0.5% except for ammonia which is 2.0% and CO which is 1.0% in addition to 0.5% b. 32 liters per minute continuous flow c. 50 ± 5% relative humidity 2. *At High Concentration and High Flow Rates* a. 2%; except for chlorine and ammonia which are 3.0% b. 64 liters per minute continuous flow c. 50 ± 5% relative humidity	1. *For Chloropicrin, Hydrogen Cyanide and Phosgene* a. See above for concentration of these test gases b. 32 liters per minute continuous flow c. 50% relative humidity 2. *For Cyanogen Chloride and Arsine* a. See above for concentration of these test gases b. 50 liters per minute intermittent flow c. 80% relative humidity
Temperature of Test and and Other Special Conditions	a. Room (about 25°C.) b. Chemical stability test conducted by equilibrating canisters for six hours at low (25%) and high (85%) humidities at 64 liters per minute and then tested against gases	a. Room (about 25°C.) b. Chloropicrin gas test run on charcoal before and after rough handling test and after rough handling on canister c. Cyanogen chloride test run on charcoal after accelerated aging
B. *Particulate Test*		
Test Particulate; Flow Rate and Time of Test	1. *Test 1* a. Tobacco smoke, a solid particulate b. 85 liters per minute continuous flow c. 5 minutes 2. *Test 2* a. DM, a solid particulate b. 32 liters per minute continuous flow c. 5 minutes	a. Dioctyl phthalate (DOP), a liquid particulate b. 32 liters per minute continuous flow c. About 5 to 10 seconds
C. *Inhalation Air Resistance* Flow Rate	a. 85 liters per minute continuous flow	a. 85 liters per minute continuous flow

TABLE III

Performance Standards and Tests for Facepiece and other Components as given in Bureau of Mines Schedule 14F

A. *General Standards*
1. *Materials*
   a. *Suitability:* Shall be suitable for the purpose they must serve; this applies to the fabric, rubber, metal, chemical, and other parts.
   b. *Irritancy:* All parts that come in contact with the skin shall be of nonirritating composition.
   c. *Sterilization:* Shall be capable of withstanding repeated sterilization treatments.
2. *Design and Construction*
   a. *Suitability:* Shall be suitable from the standpoint of safety of the wearer; freedom of movement; field and clearness of vision; fit of facepiece; and comfort.
   b. *Replaceability:* Canisters and all other parts of necessarily short life shall be easily replaced, and the tightness of the apparatus after such replacement shall be such as to assure against leakage in a contaminated atmosphere.

B. *Specific Standards*
1. *Facepiece*
   a. *Fit:* Shall assure a quick, gastight fit on persons of widely varying facial shapes and sizes.
   b. *Eyepieces:* Shall be of non-shatter type; shall be so located to provide satisfactory field of vision for persons of widely varying facial shapes and sizes; air flow shall be such as to inhibit accumulation of moisture on eyepieces.
   c. *Exhalation Valve:* Shall be guarded to prevent distortion and injury.
   d. *Head Harness:* Shall be adjustable and replaceable.
2. *Breathing Tube:* Shall permit free head movement; shall not close off by kinking or by chin or arm pressure.

C. *Tests*
1. *Tightness:* No ammonia shall be detected by the wearers when exposed in a gas chamber under the following conditions:
   a. *Concentration of Gas (Ammonia)*—1% by volume.
   b. *Time of Exposure*—10 minutes.
   c. *Activities of Wearers During Exposure:*
      (1) Walking, turning head, dipping chin—5 minutes.
      (2) Pumping air with tire pump—5 minutes.

TABLE IV

Pertinent Tests for Complete Facepiece, Component Parts, and Complete M9A1 Gas Mask as Given in Applicable Chemical Corps Specifications

Facepiece Component Part, Complete Facepiece, or Complete Gas Mask	Pertinent Tests
A. *Facepiece Component Parts*	
1. *Faceblank* (Specification MIL-F-10135B, 2 March 1955)	a. *Physical Properties of Rubber* before and after oven-aging including (1) tensile strength (2) ultimate elongation (3) permanent set (before aging only) (4) tensile stress (5) hardness (6) tear resistance b. *Toxicity*
2. *Nosecup* (Specification MIL-N-10130A, 11 May 1954)	a. *Physical Properties of Rubber* before and after oven-aging including (1) tensile strength (2) ultimate elongation (3) permanent set (before aging only) (4) tensile stress (5) tear resistance b. *Toxicity*
3. *Eyelenses* (Specification MIL-L-10114, 2 February 1950)	a. *Transmission of Light* b. *Prismatic Effect and Refractive Power* c. *Distortion*
4. *Outlet Valve* (Specification MIL-V-10134A, 4 June 1952)	a. *Resistance to Air Flow* b. *Leakage*
5. *Headharness* (Specification MIL-H-10120A, 5 December 1951)	Only generalized performance requirements and tests are given
B. *Complete Facepiece* (Specification MIL-F-10117A, 4 February 1953)	a. *Eyepiece Assembly Leakage* b. *Outlet Valve Assembly Resistance* c. *Outlet Valve Assembly Leakage* d. *Adhesion of Nosecup to Faceblank*
C. *Complete Gas Mask* (Specification MIL-M-10121, 3 February 1950)	No performance requirements or tests are prescribed

TABLE V

Performance Standards and Tests for Complete Gas Mask as Given in Bureau of Mines Schedule 14F

Mask Referenced in Bureau Mines Schedule 14F	Man Tests						Machine Tests	
	Gas Test Requirements						Air resistance[D]	
	Test Gas	Min. conc. of test gas	Max. Conc. of test gas	Activity of wearer. Exercise and activity in minutes[B]	Total req'd time of protection[C]	Particulate test requirement	Inhalation	Exhalation
		%	%		minutes		mm H_2O	mm H_2O
TYPE A, Acid Gas Mask	Specific gas for which approval is requested	2	1, (except HCN, which is 2%)[A]	1. Walking vigorously for 5 minutes. 2. Sitting at rest for 5 minutes. 3. Stationary running and arm movements for 10 minutes. 4. Sitting at rest for 5 minutes. 5. Pumping air with hand tire pump for 5 minutes.	30	*Test No. 1* Shall provide protection to wearer for 10 minutes in a room filled with smoke from smudge-burning of 1 lb. cotton waste.	3.5	1.25
TYPE B, Organic Gas Mask	Specific gas for which approval is requested	2	2		30		3.5	1.25
TYPE C, Ammonia Gas Mask	Ammonia (NH_3)	3	3		30	*Test No. 2* Shall provide protection to wearer for 20 minutes *with canister connected to room* in which there is atmosphere of 500 ppm by volume of tin tetrachloride in air.	3.5	1.25
TYPE D, Carbon Monoxide Gas Mask (for regular service)	Carbon monoxide	2	2		30		3.5	1.25
TYPE N, Universal Gas Mask	Acid gas	2	1, (except HCN, which is 2%/[A])	Exercises 1, 2, & 3 (see above) for 5 minutes each.	15			
	Organic gas	2	2	Exercises 1, 2, 3, 4 & 5 (see above) for 5 minutes each.	25		3.75	1.25
	Ammonia gas	3	3	Exercises 1, 2 & 3 (see above) for 5 minutes each.	15			
	Carbon monoxide gas	2	2	Exercises 1, 2, 4 & 5 (see above) for 5 minutes each; exercise 3, for 10 min.	30			

[A] In the case of HCN, the wearer will wear the complete mask in the test atmosphere for 1 minute; and immediately following this test will be continued with the canister of the mask attached to a source of the test atmosphere with the wearer in uncontaminated air.

[B] Average breathing rate of wearer while wearing mask and performing the exercises will be about 25 liters per minute.

[C] To meet the requirements of these tests, the masks shall provide protection to the wearers for the indicated time such that the wearers will receive no ill effects; shall not experience excessive fogging; or cause undue discomfort.

[D] Air resistance tests made with air flowing at rate of 85 liters per minute.

TABLE VI

Engineering and User Tests Conducted to Evaluate Operational Suitability of M9A1 Mask

A. *Laboratory Type Tests*
  1. *Overall Mask Evaluation*
    a. Fitting Trials
    b. CW Gas Chamber Trials
    c. BW (Bacillus Globigii) Aerosol Chamber Tests
    d. Simulated Tropical Chamber Tests
    e. Simulated Desert Chamber Tests
    f. Simulated Arctic Chamber Tests
    g. BW, CW and RW Decontamination Tests
    h. Voice Transmission Tests
    i. Vision Tests
    j. Water Immersion Tests
    k. Physiological Strain Tests
    l. Inhalation and Exhalation Resistance
    m. Compatability for Use by Personnel Wearing Spectacles
    n. Combat Course Traversal
  2. *Mask Component Evaluation*
    a. *Canister Evaluation*
      (1) BW (Bacillus Globigii) Aerosol Tests
      (2) CW Gas Tests
      (3) Radioactive Methylene Blue Aerosol Test
      (4) Radioactive Sodium Iodide Test
      (5) Radioactive Sulfur Dioxide Gas Test
      (6) Water Resistance Tests
      (7) Tropical Chamber Surveillance Tests
      (8) Desert Chamber Surveillance Tests
      (9) Arctic Chamber Surveillance Tests
    b. *Facepiece (Including Faceblank, Eyelens, Headharness) Evaluation*
      (1) Liquid CW Agent Pentration Tests
      (2) Skin Toxicity Tests
      (3) Eyelens Fogging
B. *Field Type Tests*
  a. Comfort
  b. Donning Time
  c. Interference with Firing of Weapons
  d. Durability under Field Use Conditions
  e. Interference with Normal Vision
  f. Interference with Normal Speech Transmission
  g. Wear Tolerance under Hot-Wet (Tropical) Conditions
  h. Wear Tolerance under Hot-Dry (Desert) Conditions
  i. Wear Tolerance under Wet-Cold Conditions
  j. Wear Tolerance under Cold-Dry (Arctic) Conditions
  k. Wear Tolerance under Temperate Conditions
  l. Interference with Telephone and Radio Speech Transmission
  m. Interference with Use of Optical Instruments
  n. Durability of Effects of Rain and Mud
  o. Durability to Withstand Water Immersion
  p. Wear Tolerance under Heavy Work Conditions
  q. Compatability Trials with Army Environmental and Protective Clothing and Equipage
  r. CW Gas Tests
  s. BW Aerosol Tests
  t. Compatability with Use of Army Equipment
C. *Environmental Surveillance and Operational Tests*
  a. *Cyclic Surveillance and Functioning Tests* after Surveillance under
    (1) Tropical (Panama) Conditions
    (2) Desert (Yuma, Arizona) Conditions
    (3) Temperate (Edgewood, Md.) Conditions
    (4) Arctic (Big Delta, Alaska) Conditions

Corps in their specifications covering the purchase of the mask. As mentioned previously, extensive laboratory and operational suitability testing is conducted on the masks during their development. The specifications for the component parts of the masks, if complied with, are generally held to insure the acceptability of the purchased item.

To illustrate the types of tests which the Chemical Corps has used to evaluate the acceptability of the M9A1 mask during the development period, data are presented in table VI. Tests are conducted on combat obstacle courses, in actual field maneuvers and under every conceivable climatic condition to insure the acceptability of the developed mask. Additional testing has been made to insure the acceptability of the mask and its components against bacteriological warfare (BW) and radiological warfare (RW) agents under laboratory and/or field conditions. Also, extensive wear tests have been conducted under a wide variety of work conditions, to insure the acceptance of the mask by the potential wearer.

IV. Summary

In summary, it can be stated that within the limits of the objectives for which the Bureau of Mines schedules and the Chemical Corps specifications can be compared, there is some general similarity in the gas tests and air resistance tests. The Chemical Corps test for insuring efficiency of particulate removal is generally held to provide a superior filter. Bureau of Mines schedule calls for only generalized requirements for the facepiece and other components, but extensive man tests for the complete mask. Conversely, the Chemical Corps prescribes detailed tests for the facepiece and other components, but no tests for the complete gas mask. The Chemical Corps mask has been subjected to extensive evaluation during its development.

Respiratory Protection Equipment Developments by the U. S. Army Chemical Corps

ALLAN L. WEST

Protective Development Division, U. S. Army Chemical Warfare Laboratories, Army Chemical Center, Maryland

In addition to its mission of developing respiratory protective equipment for protection of the United States armed forces against the hazards of toxicological warfare agents, the U. S. Army Chemical Corps has the responsibility for the procurement, storage, and issue of several types of safety and rescue type respiratory protective equipment for use by agencies of the Department of Defense. An illustrated discussion is presented on the following classes of individual respiratory protective equipment which have been standardized by the U. S. Army Chemical Corps: military protective masks, special purpose gas masks, self-contained breathing apparatus, dust masks and paint spray respirators. Also discussed are two (2) experimental protective masks developed by the Chemical Corps for the Federal Civil Defense Administration. The procedures used by the Chemical Corps in undertaking the development and testing of new items of respiratory protective equipment are briefly described.

SINCE ITS establishment as a separate branch of the Army in 1920, the U. S. Army Chemical Corps, or Chemical Warfare Service as it was then known, has had as one of its major missions, the development, procurement, and supply of equipment for providing respiratory protection for the U. S. Armed Forces against the effects of toxicological warfare agents. To fulfill this mission, the Chemical Corps established experimental laboratories at what is now the Army Chemical Center in Maryland. Over the past 37 years, a continuous program of research and development has been carried out in these Laboratories and by contractors to develop efficient and improved adsorbents, filter materials, testing procedures, and gas masks for military use. Because of its eminence in this field, the Chemical Corps has been frequently called upon to develop special respiratory protective devices to cope with respiratory hazards outside of the field of chemical warfare because the required devices were not commercially-available. It is the purpose of this paper to review some recent Chemical Corps developments in this field and to indicate their use throughout the military establishment.

Under recent directives [1, 2] of the Department of Defense, the U. S. Army Chemical Corps has been assigned all logistic responsibilities for military respiratory protective devices assigned to the Department of Defense. Under this responsibility, the Chemical Corp is charged with the preparation of specifications, procurement, storage, issue, and maintenance of those military respiratory protective devices which have been type-classified as standard types to meet established military requirements. According to current definition, respiratory protective equipment for military use is defined as being those items, regardless of their source of procurement, which are issued to personnel of the military establishment upon Tables of Organization and Equipment or other authorized basis to enable them to accomplish their mission.[3]

When a military requirement for an item has been approved by the Chief of Research and Development, Department of Army, a set of performance or military characteristics for the item is prepared. After they have been coordinated with the various using services and the interested technical services who will be required to develop the item, the military characteristics are approved as a basis for selecting the most desirable item to meet the military requirement.[4]

The military characteristics are much more rigorous with regard to ruggedness and performance at temperature extremes for an item of equipment which is required for protection against chemical warfare agents out-of-doors in combat than for a similar device which is intended for protection against irritants and fumes in arsenals located in temperate regions.[5] Thus, a gas mask for combat use must be capable of

FIGURE 1. M3 lightweight service gas mask

satisfactory performance at temperatures of −40°F or lower while an ammonia mask would rarely be required to operate at temperatures below freezing. Due consideration is given to the need for special performance requirements of this nature before a military respiratory protective device is type-classified as a standard type to fulfill a military requirement. If a military requirement is established for a respiratory protective device for which there is no commercial source, the Chemical Corps may either undertake the development of a suitable item or modify a commercial item to enable it to fulfill the military characteristics.

From 1917 until 1946, the standard Army gas mask as developed by the Army Chemical Corps has consisted of a rubber facepiece to which was attached a corrugated rubber tube leading to a conventional air-purifying canister located in a canvas carrier. The M3 lightweight service gas mask shown in Fig. 1 is typical of this type of military gas mask. It has a molded rubber facepiece and curved plastic eyelenses held in place by pronged metal eyerings. Inside the facepiece is a soft molded rubber baffle known as a nosecup which makes contact over the wearer's nose and serves to prevent exhaled air from passing over the eyelenses.[6] This is especially important in order to prevent frosting of the eyelenses when the mask is worn at subfreezing temperatures.

When preparations for the assualt on the Continent of Europe began in 1943, the Chemical Corps was called upon to develop a special assault gas mask with minimum weight and bulk to be carried only by the initial waves of troops. This new mask was created by removing the hosetube from the facepiece of the M3 mask and attaching an M11 combat canister directly to the facepiece as shown in a cut-away view in Fig. 2. This new canister was patterned after British and German axial-flow canisters in which the air passes first through an aerosol filter made of

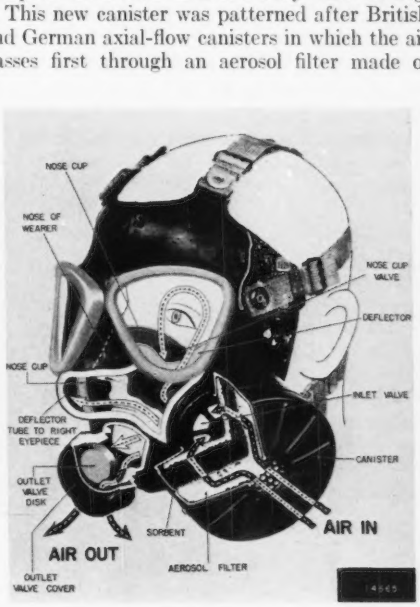

FIGURE 2. M9 combat gas mask

pleated asbestos-bearing filter material, then through a 1-⅛ inch bed of specially impregnated activated charcoal. Since it was obvious that this cheek-mounted canister contained less charcoal than the canister used with hose-type masks, the M11 canister was made of aluminum instead of steel to reduce its weight and was provided with threads so that it could be readily removed from the facepiece and replaced with a fresh canister in the field if the need should arise. Because of the advantages created by the removal of the hosetube, this mask, which was originally known as the assault gas mask, was renamed as the M9 combat gas mask and type-classified in 1946 as the standard-type mask for use by all components of the U. S. Army. Concurrently the M3A1 mask was reclassified as a limited standard item to be used in training. Like the M3 gas mask, the M9 gas mask had three (3) sizes of facepieces to assure a proper fit on the adult male military population. Extensive tests conducted with the M9 mask showed it to be capable of providing protection against chemical warfare irritant smokes, biological warfare spores, and radioactive dusts, in addition to chemical warfare agents in gaseous form. Thus, the M9 mask was seen to overcome potential requirements for special military masks for protection against biological warfare or radiological warfare agents. After it had been provided with laminated glass lenses and a simplified carrier, the M9 mask was given the name of M9A1 field protective mask to denote that it would provide respiratory protection against all chemical, biological, and radiological agents which might be encountered in military operations.[7] The M9A1 mask is still the standard type for use by the U. S. Army, U. S. Air Force, U. S. Marines, and land-based Naval installations.

When the Manhattan District began its work during World War II on the purification of uranium compounds and other radioactive materials in the development of the atomic bomb, a requirement arose for a special aerosol filter canister of high protection efficiency which could be used with a standard gas mask. A very high degree of protection was desired because of the extreme health hazards associated with breathing or ingestion of the radioactive particulates which were generated during the processing operations. A further requirement for a high efficiency aerosol filter canister was indicated for the U. S. Army Biological Warfare Laboratories at Ft. Detrick, Maryland, where investigations of BW agents were being carried out during World War II. The needs of the Manhattan District and Ft. Detrick were met by using the M9 mask facepiece and replacing the M11 canister with the M14 gas mask aerosol canister (previous designation: E4R5 aerosol filter). This canister is one in which two (2) standard Chemical Corps aerosol filters, Fig. 3, are arranged in series in a shortened M11 canister body as shown in Fig. 4. The current specification[8] for this canister requires that it will allow not more than one (1) part in 100 thousand of dioctyl phthalate aerosol particles[9] to pass. Since this value represents the least amount of penetration which can be measured by the existing testing device it is apparent that the canister may be many times more efficient than the specification implies. The canister is provided with a threaded receptacle on the influent side, thus allowing it to be installed in air lines and vents leading from equipment con-

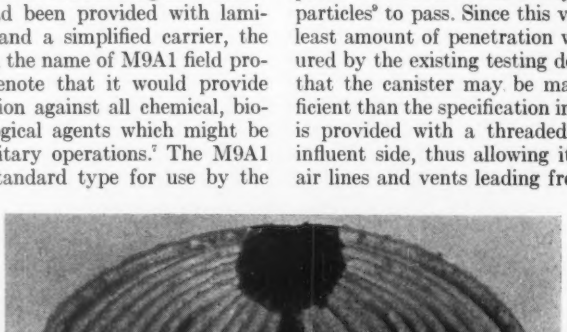

FIGURE 3. Shell-type pleated aerosol filter element.

FIGURE 4. E4R5 gas mask aerosol filter

taminated with radioactive materials in addition to its use on the mask. Since 1946, the Chemical Corps has manufactured and shipped approximately 30 thousand double-filter aerosol canisters to the Atomic Energy Commission and the U. S. Army Biological Warfare Laboratories for use in their respective safety programs.

When persons are required to work in areas containing an appreciable quantity of highly toxic airborne particulates, they are frequently provided with a hood that is an accessory to the M9A1 field protective mask. The M3 toxicological agents gas mask hood,[10] in Fig. 5, is made of impermeable fabric and prevents the deposition of particulates in the hair and in the headharness of the mask where they could be disturbed and shaken off to become a secondary respiratory hazard, when the mask is removed. Furthermore, since the hood covers the entire mask except the eyelenses and canister inlet, it serves as a reservoir to collect the purified air which is exhaled through the outlet valve of the mask. Thus, the entire face-fitting surface of the mask is enveloped in a curtain of uncontaminated air, and should minor leaks in the faceseal result from facial irregularities, or growth of beard, only uncontaminated air would enter the mask. Such a hood is generally used as a component of the M3 impermeable protective outfit[10] by Chemical Corps personnel engaged in field trials and in the manufacturing and handling of toxic agents and has proved highly successful in eliminating any casualties due to leakage of the mask. When the worker emerges from the contaminated area he is showered down with water to remove any contaminated materials which may have deposited on the outside of the hood so that when the mask and hood combination is subsequently removed, these will be no hazard from aerosol shake-off.

While the M9A1 field protective mask was generally suitable for most military type operations, it had certain shortcomings which were unacceptable to personnel in the Army Tank Corps. The side-mounted canister interfered with the use of the sighting devices in the close quarters inside the tanks and the rigid eyelenses did not meet the tank commander's requirements for the use of binoculars. Furthermore, the breathing resistance of the canister was deemed excessive in view of the high work rate required for the gun loaders during military operations. To meet this requirement, the Chemical Corps developed the M14 tank protective mask[11] which is shown in Fig. 6. This mask incorporates a flexible one-piece plastic eyelens which will permit the binoculars to be pressed close to the eyes and a microphone which can be plugged into the tank intercommunication system. The canister has been removed from the facepiece and placed at the end of the corrugated hosetube and is provided with the male portion of a quick disconnect coupling by which it can be connected to a special air-purifying device which forces purified air through the canister into the mask.

As mentioned previously, the Chemical Corps has been given complete logistic responsibility, not only for the combat-type masks described above, but also for a number of special gas masks which are required by the Military Services in

FIGURE 5. M3 impermeable protective outfit

connection with various phases of their missions. These items, for the most part, are not intended for use in front line combat with the enemy, but are intended for use against special hazards associated with supporting operations. For example, the Chemical Corps has standardized the M10 acid and organic vapors gas mask for use by workers handling volatile chemicals in Government arsenals, the M11A1 all-purpose gas

FIGURE 6. M14 tank protective mask

mask for use by firefighting crews, and the M12 ammonia gas mask for use by refrigeration specialists.[12, 13] The specifications for the M10, M11A1 and M12 gas masks are designed around commerically-available gas masks which comply with the applicable schedules of the Bureau of Mines approval schedules for respiratory protective devices. The M12 ammonia gas mask shown in Fig. 7 is typical of a commercial item which meets Chemical Corps requirements for special purpose masks. A fairly complete listing of manufacturers of Bureau of Mines approved special purpose gas masks is given in a Department of Army Technical Bulletin, TB-MED 223, Respiratory Protective Devices, dated 13 September 1951.

Two (2) types of self-contained breathing apparatus have been type classified by the Chemical Corps for personnel who may be required to handle bulk quantities of rocket propellants such as red-fuming nitric acid and aniline in locations where the concentration of the fumes in the air may exceed 2 per cent by volume, thus causing conventional masks to be unsafe. The M13 oxygen-generating breathing apparatus shown in Fig. 8 provides a respirable oxygen-air mixture for approximately 45 minutes from a replaceable canister.[12, 13] This breathing apparatus is of a commercial design which meets the requirements of the Bureau of Mines Approval Schedule 13C. The device is mounted on the wearer's chest, thus making the unit ideal for use in emergency rescue operations where per-

FIGURE 7. M12 ammonia gas mask

FIGURE 8. M13 oxygen-generating breathing apparatus.

sonnel may have to be carried out on the rescuer's back. However, in the case of personnel engaged in the filling of guided missiles with propellants, the bulk of the M13 breathing apparatus on the chest is a disadvantage in that it interferes with certain forward manipulations. Accordingly, since self-contained breathing apparatus is used mainly by personnel servicing guided missiles, the Chemical Corps type-classified the M15 compressed air breathing apparatus shown in Fig. 9 is a standard type which provides respirable air for approximately 30 minutes.[13] The M13 oxygen-generating breathing apparatus was simultaneously made a limited standard type for use until stocks on hand become unserviceable and can be replaced with the M15 apparatus. This apparatus is similar to commercial-type compressed air underwater breathing apparatus which has been modified by the addition of the M9 facepiece which includes a nosecup, since no commerical facepieces are currently provided with nosecups. This modification was made in order to make the apparatus operable at temperatures down to as low as −40°F. since the M9 facepiece can be fitted with a standard winterizing kit which enables it to be worn at extremely low temperatures without undue discomfort or eyelens frosting.

FIGURE 9. M15 compressed-air breathing apparatus.

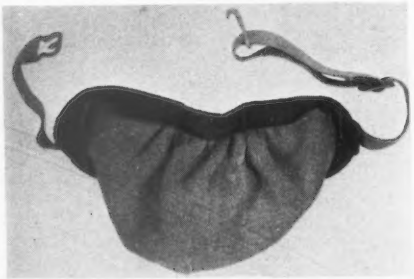

FIGURE 10. M4 air-filtering dust respirator

The clouds of dust raised by the military vehicles in combat and training operations during World War II caused such discomfort that a military requirement was established for a special dust respirator for use by truck drivers and other personnel required to work where large amounts of coarse dust are encountered. The item developed by the Chemical Corps to meet this requirement was the M4 Air Filtering Dust Respirator, shown in Fig. 10. The device consists of a piece of napped knitted fabric provided with a head and neck strap. A malleable aluminum strip is included in the body of the respirator so it can be formed to give a tight fit on the wearer's nose.[12] The M4 dust respirator meets the military requirements that it should give a good fit on a wide range of face sizes, it should not weigh more than one ounce and should withstand numerous washings without damage.

In response to a requirement generated in the Army Ordnance Corps, the Chemical Corps was requested to develop a paint spray respirator for use in Ordnance shops where ordnance vehicles are renovated and painted. Since no available commerical respirators were acceptable, the Chemical Corps modified a commercial 2-cartridge half-mask respirator as shown in Fig. 11 by filling the cartridges with Chemical Corps impregnated activated charcoal and adding a sheet of Chemical Corps type 5 asbestos-bearing filter material as a prefilter for obtaining the desired particulate protection. This item was standardized as the M5 Air Filtering Paint Spray Respirator.[13]

In 1948 the Chemical Corps was authorized by the Research and Development Division, Department of Army, to develop a low cost noncombat protective mask for use by civilian employees and dependents of U. S. Armed Forces personnel at U. S. military installations on foreign soil. The resulting mask, the E51R15 noncombat protective mask, shown in Fig. 12, consists of a rubber coated fabric facepiece with a cemented-in plastic eyepiece and the M11 combat canister screwed into a receptacle in the snout position.[13] The mask is made in six (6) sizes sufficient to fit individuals from 4 years old through adults. It provides equivalent toxicological protection to that afforded by the M9A1 field protective mask, but at about 40 per cent of the cost. However, it is not as rugged as the M9A1 mask nor will it operate at as low temperatures before frosting of the eyepieces will occur. Although the Department of Army withdrew its requirement for this mask in 1955, the design was determined to meet the requirements

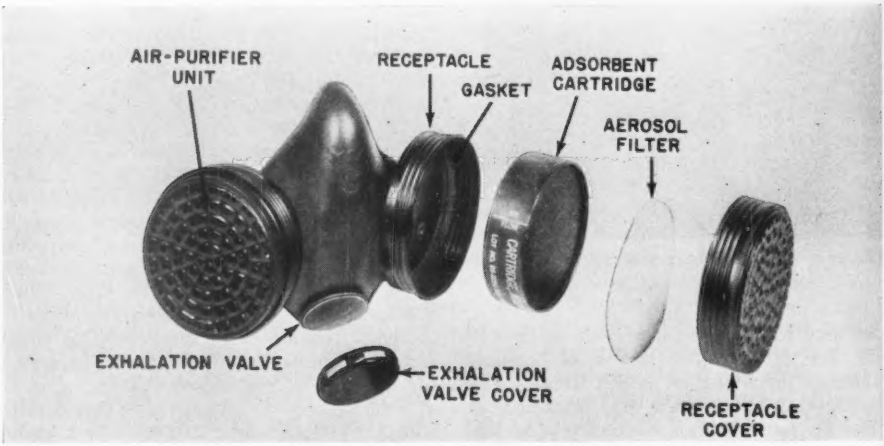

FIGURE 11. M5 air filtering paint spray respirator

FIGURE 12. E51R15 noncombat protective mask

of the Federal Civil Defense Administration for use by key civil defense employees such as Area Wardens, Auxiliary Firemen, Salvage Crews, and Control Center Workers. The Chemical Corps is currently manufacturing a limited quantity of this mask in three (3) adult sizes for FCDA. The Chemical Corps effort on the development of a prototype civilian protective mask to meet the unfulfilled military requirement which was approved in 1951 has culminated in design of the E52R26 civilian mask, shown in Fig. 13. This mask is intended for use by the civilian population of the U. S. in the event of toxicological warfare attack and is made in six (6) sizes to fit individuals from 4 years up and older. It is not provided with a replaceable canister, but incorporates a combination gas and aerosol filter medium, specially developed by the Chemical Corps, in the facepiece which is made from a special grade of polyvinyl chloride plastic. The plastic periphery is formed to the filter material during an injection molding process which forms a flat faceblank. After the clear plastic eyelenses are heat sealed into the faceblank, the mask is formed by folding the faceblank down the middle and

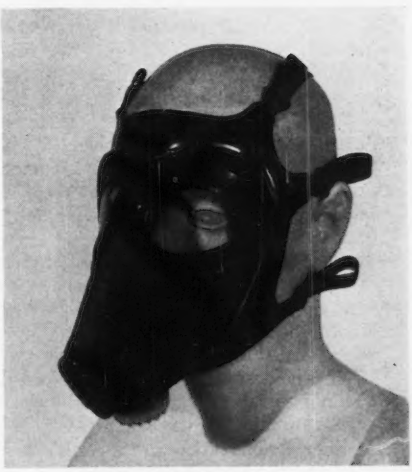

FIGURE 13. E52R26 civilian protective mask

heat-sealing under the chin.[13] A simple vulcanized fiber baffle which is inserted inside the facepiece deflects the incoming air flow inside of the eyepieces to discourage eyelens fogging and

also serves to deflect the exhaled breath out through a low-cost outlet valve which is located in the underchin position. The development of this civilian mask is currently being carried out with funds provided by the F.C.D.A. since the Department of Army no longer has a military requirement for such a mask. However, the mask provides protection equivalent to that of the M9A1 field protective mask against aerosols and is designed to meet the current F.C.D.A. requirements for an evacuation-type protective mask which will afford sufficient protection against gases to permit personnel to reach shelters or to evacuate contaminated areas. The mask is provided with a simple plastic carrier and should cost between $2.00 and $2.50 when put into mass production.

It can be seen from the foregoing that the Chemical Corps has developed and type-classified a variety of protective masks, breathing apparatus, and respirators for providing respiratory protection against toxicological agents, industrial fumes and aerosols, and nuisance dusts.

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Industrial Noise Manual

This manual presents a comprehensive coverage of noise, its evaluation and control. Among other things, the manual covers such subjects as the physics of sound, sound transmission, measurement of sound, instruments, techniques, procedures for making sound surveys, calibration of instruments, how we hear, effects of noise, why we don't hear, measurement of hearing, medical control and hearing conservation, engineering control of noise and personal protective measures.

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The Respirator Problem—an Industrial Hygienist's Viewpoint*

HARRY S. JORDAN

Los Alamos Scientific Laboratory, University of California, Los Alamo, New Mexico

RESPIRATORY protective equipment is an industrial hygiene or a safety engineering tool that is obviously here to stay. In fact, since the advent of the atomic energy industry and the introduction of the newer types of pesticides, such equipment has been and will continue to be used on an increasing scale. The fact that it is a well established and sound industrial hygiene practice to use respirators only as a last resort[1-3] perhaps is responsible for a sense of uneasiness on the part of individuals prescribing their use; for an individual rarely can be sure what constitutes a last resort. A more clever individual might engineer or sell a better solution to the problem.

In addition, the use of a respirator is not an engineered solution for any problem and its effectiveness cannot readily be determined or predicted over any period of time. As a corrective measure, therefore, respiratory protective equipment is, at best, a second choice and this probably accounts, at least in some measure, for the lack of interest on the part of most industrial hygienists in the respiratory protective equipment field. This lack of interest on the part of industrial hygienists has permitted the growth of certain problems in the field that now require their attention.

It should be stressed that these problems are largely the result of our lack of interest, for in describing the problems the existing program in the respiratory protective equipment field will be criticized. By implication, the Bureau of Mines and the manufacturers will be criticized since they have the only program in the field. It is firmly believed, however, that these problems would not exist today if, in the past, industrial hygienists had given their utmost support and encouragement to the Bureau of Mines and had extended their most intelligent cooperation to the manufacturers.

Approval Limitations

The first problem arises from the fact that the Bureau of Mines does not have the authority, or has not chosen, to assume a definite responsibility for evaluating all respiratory protective equipment available on the open market.

At the present time, the Bureau of Mines has schedules detailing tests for permissibility for only five classes of respiratory protective equipment, namely; (a) filter type, dust, fume, and mist respirators for materials not significantly more toxic than lead;[4] (b) supplied-air respirators;[5] (c) non-emergency gas respirators for organic vapors;[6] (d) gas masks;[7] (e) self- contained breathing apparatus.[8]

Schedules are not in effect for the following types of respiratory protective equipment: (a) filter type respirators for protection against materials significantly more toxic than lead, specifically for protection against beryllium, the new pesticides, and radioactive material; (b) paint spray respirators; (c) chemical cartridge respirators for protection against gases and vapors other than organic vapors; (d) escape-type, self-contained breathing apparatus; and (e) combination airline and self-contained breathing apparatus. In the latest catalogues of major manufacturers of respiratory protective equipment, fully 50 per cent of the items are not Bureau of Mines approved, either because there is not an applicable schedule or because the item does not conform to Bureau of Mines requirements. Unfortunately, if a device lacks an approval, it is not readily apparent whether this is due to the lack of a suitable schedule or to its inability to be approved under an existing schedule.

This incomplete coverage by the Bureau of Mines makes it necessary or desirable for other agencies to establish separate evaluation programs. Individuals in close contact with the field are in general agreement that for a number of reasons a multiplicity of approving agencies would be highly undesirable. However, the Department of Agriculture has already entered the field[9, 10] and the possibility of the Atomic Energy Commsission establishing a separate program cannot be ignored.

Another aspect of the problem is that it is certainly to our interest as industrial hygienists that the Bureau of Mines approval gains the

* Work done under the auspices of the Atomic Energy Commission.

highest possible prestige and widest acceptance, yet it would be only natural for the prestige and general acceptance of any approval to be reduced if the approval program only covered a portion of the items available on the market.

Approval vs Rating System

The second problem is related somewhat to the first problem, and that is the problem created by an approval system rather than a rating system. This is a complex problem that admittedly cannot be handled adequately in a limited time, but it is believed some thought should be given to the matter. In the first place, an approval is comparable to a go-no-go gauge, in that it does not distinguish between items of high standards and items merely satisfying minimum requirements. Personnel at the Bureau of Mines have an abundance of data regarding relative merits of various respirators but this information is withheld in order to preserve the confidential relationship between the manufacturers and the Bureau, necessary under an approval system. The rather limited rating of respirators conducted by the University of Rochester[11] during the last war in indicative of the type of information that would be available in even greater detail, if respirators were subjected to a rigorous rating system.

Another aspect of an approval system is the natural tendency for an approval system to be extremely conservative. Professors Drinker and Hatch[2] in the second edition of their book *Industrial Dust* question the practice of the Bureau of Mines in refusing to approve mechanically operated blowers for men wearing hose masks in atmospheres immediately dangerous to life. On the other hand, individuals responsible for approving a device will naturally be conservative and will insist that the approval indicates that devices will operate satisfactorily under severe or even somewhat improbable conditions.

An anticipated difficulty along these lines is that if respiratory protective devices are approved for protection against radioactive material, they also will be evaluated under conditions of severe exposure and the approved respirator, in all probability, will not be a simple device. This means that for anticipated severe exposures the approved device would be worn, but in accordance with the general practice at many AEC installations a simpler non-approved respirator would be used a great proportion of the time for routine exposure. Such a situation would be undesirable and fraught with legal and labor difficulties.

Inertia in Basic Research

The third problem in the field is the lack of basic research and development in the respiratory protective equipment field. It is sincerely believed that a review of the literature in this field would convince anyone of this lack of basic research.[12] With the major exception of Dr. Leslie Silverman's[13-17] splendid study for the Office of Scientific Research and Development on Fundamental Factors in the Design of Protective Respiratory Equipment, very little basic information on the physiology or mechanical developments involved in respiratory protection has been reported in the American literature. It is possible, but hard to believe, that really worthwhile studies are being accomplished but are not being reported.

In tracing the development of respiratory protective equipment,[18] it becomes evident that the basic knowledge in the field and major improvements for civilian respirators are the result of developments for warfare. The following statement appears in the American Standards Association[19] Safety Code for the Protection of Heads, Eyes and Respiratory Organs, No. Z2-1938: "The development of gas masks was carried on intensively during the war, and at its conclusion the results were applied to masks for industrial purposes."

This statement refers of course to WW I, but it is also perfectly true today regarding WW II. The depressing aspect of the matter is that, as matters stand today—some twelve years since the last war, industrial workers can expect little improvement in their respiratory protective devices until after the next war. And in the next war, if such occurs and we are again afforded the necessary time, our nation once more will divert sorely needed research personnel and facilities to up-date our knowledge and equipment. Not a single soldier owes his life or health to the proper use of the gas mask in the last war.

On the other hand, the total economic loss and number of personal tragedies brought about by the death and impaired health of industrial workers breathing harmful industrial substances is overwhelming and impossible of calculation. Obviously, this loss and suffering did not result from the use of improper respirators; the point is that the task of protecting workers from inhalation hazards requires the daily use of a great number of respirators and this demand justifies our best research efforts. The armed forces should be the recipient of the benefits of research directed towards improv-

ing respiratory protective equipment for civilian workers, rather than the reverse.

The manufacturers of respiratory protective equipment have had ample opportunity to develop a suitable research program in this field. The fact that their personnel have not contributed to the literature or to major developments in the field is evidence that the research activities which the manufacturers are capable of supporting are not adequate.

Revision of Approval Schedules

The fourth problem is the matter of discrepancies or debatable items in the Bureau of Mines existing approval schedules. To criticize the Bureau of Mines schedules, in view of our debt to the Bureau for improving the quality of respiratory protective devices, would appear to border on complete ingratitude. Therefore, it is stressed again that the lack of organized effective interest on the part of industrial hygienists is probably the reason why the present schedules include items with which we may not be in complete agreement.

As an example, it should be realized that revision of the Bureau of Mines schedules do not require compliance with the terms of the revision within any specified time. In other words, once a device has been issued a Bureau of Mines approval it retains that approval indefinitely, even if the schedule under which it was approved has undergone four or five revisions.[20] Furthermore, the device may undergo definite major modifications, but retain the old approval by simply having the approval extended. It is even possible to finally have two rather completely different respirators carrying the same Bureau of Mines approval. The approval is extended on the basis of drawings and tests deemed necessary by the Bureau of Mines, but presumably under conditions specified by the schedule in effect at the time of the original approval.

The Los Alamos Scientific Laboratory's Technical Library, after a determined and persistent effort, has been able to secure copies of the old schedules from the Bureau of Mines. However, some of the schedules are available only on a library loan basis and the only schedules readily available are the schedules adopted in 1946 and 1955. Certainly less than 5 per cent of the devices now on the market are approved under the latest schedules. Actually some devices listed in the latest catalogues of major manufacturers carry Bureau of Mines approval issued in 1928 under schedules adopted in 1925. Ordinarily, one would expect that a device approved 20 or 30 years previous to the issue date of the latest approval schedule would not satisfy the requirements of the latest schedule. This is not the case, however, in regard to respiratory equipment issued Bureau of Mines approval, for the various revisions of the Bureau of Mines schedules have not changed the requirements materially. Never the less, it is certainly to be hoped, that eventually the progress in this field, as reflected by improved standards for approval, will be such as to make it undesirable for a device to retain an approval without regard to time or improved standards.

Another item that should be examined more closely is the specification covering methods of testing the penetration and breakdown of filtering elements and the resistance on inhalation and exhalation. At the present time, penetration and breakdown are determined with a continuous air flow rate of 32 liters per minute. Resistances to inhalation and exhalation are measured at a continuous air flow of 85 liters per minute. The figures generally quoted as the Bureau of Mines' maximum allowable resistances under these conditions are 50 mm. of water for inhalation and 25 mm. of water for exhalation. As shown in Table I, however, various standards prevail for different types of respirators.

Silverman[13] comments on these figures as follows: "The basis for these figures has been found to be arbitrary. They were selected with regard to the manufacturer's ability to meet a given specification rather than as the result of any fundamental physiological study." His specific recommendation on this matter is the suggested maximum resistance of 82 mm. of water for inspiration and 53 mm. of water for expiration measured at 85 liters per minute. It should be

TABLE I

Type	Schedule	Max. Allowable Resist. mm. of H_2O at 85 liters/min.	
		Inhalation	Exhalation
Gas Masks	14F	89 (3.5″)	32 (1.25″)
Gas Masks, Type N and Special Filters	14F	95 (3.75″)	32 (1.25″)
Supplied Air Respirator Type A and AG	19B	63.5	25
Supplied Air Respirator Type B and BE	19B	38	25
Supplied Air Respirator Type C	19B	50 (4cfm)	25
Filter Type, Dust, Fume, and Mist	21A	50	25
Non-Emergency Gas Respirators (organic vapors only)	23A	50.8 (2″)	25.4 (1″)
Non-Emergency Gas Respirators (organic fumes plus dust, fumes, and mists)	23A	76.2 (3″)	25.4 (1″)

borne in mind that this specific recommendation was directed to the armed forces evaluating full face masks to be used by able bodied young men during times of stress. It is indeed questionable if these maxima should be used for evaluating respiratory protective equipment designed to meet the needs of the civilian working population with its inherent greater distribution of age, physical well being, and working stress.

The British standards[21] are ¾-in. or 19 mm. of water on inhalation and ½-in. or 12.5 mm. of water on exhalation measured at 3 cfm or 85 liters per minute. The matter of determining penetration and breakdown of filter elements and resistance on exhalation and inhalation at continuous air flows of 32 liters per minute and 85 liters per minute, respectively, is also questioned. Professors Drinker and Hatch[2] indicate that it would be better for both penetration and resistance to be measured at 120 liters per minute, preferably by means of a breather-pump technique[22] rather than under conditions of steady air flows.

The Bureau of Mines schedules do not specify details or requirements for valves for respirator protective equipment. Yet there is clear evidence in the literature of details that should be required of such valves. Guyton and Lense[23] state, "The penetration efficiencies of outlet valve assemblies vary greatly, depending upon their design and construction." Silverman,[17] in his report on the characteristics of valves, found a significant difference in valves. Drinker and Hatch[2] indicate several factors that should be evaluated in determining the suitability of valves.

At Los Alamos we have experienced complete failure with exhalation valves of an approved respirator. The failure was due to the curling of the rubber valve and its consequent inability to seat properly. Fortunately, the manufacturer has changed the type of rubber and design of the valve on later models. It should also be noted that Schedule 21A states that for filter type respirators an inhalation valve is optional. Our experience indicates that inhalation valves should be required on such respirators. The American Standards Association's Safety Code Z2-1938[19] in large measure reflects the Bureau of Mines schedules, but it does differ in this respect since it states that mechanical-filter respirators shall include an inhalation valve.

The requirements of the different schedules for face fit and comfort are not consistent, nor are the tests sufficiently objective. It seems improbable that the same adjustment of the respirator is used to evaluate face fit and comfort. Our experience has been that it would be virtually impossible to wear the respirator for any protracted period when adjusted to the same degree of tightness required to pass the face fit tests. In our opinion the necessity for two straps on any half mask respirator would have been indicated by a proper determination of face fit that was consistent with reasonable comfort.

The Bureau of Mines specifies various exercises for man-testing respirators. Certainly any prescribed exercise will give a variety of breathing patterns, depending upon the vigor with which the exercises are performed. The same individual will no doubt vary his own performance and consequent breathing pattern in accordance with his sense of well being. A more objecitve method of establishing a more uniform breathing pattern would be to specify the work rate on a bicycle ergometer. Silverman[16] has established that the breathing patterns obtained on men exercising on the bicycle ergometer at various work rates can be correlated with breathing patterns obtained on men performing various tasks.

Summary

The lack of interest on the part of most industrial hygienists has been responsible for the growth of a number of problems in the respiratory protective equipment field. It is believed these problems have been created by:

1. The lack of a fixed responsibility for the Bureau of Mines to evaluate all commercially available respirators.
2. The use of an approval system to evaluate respiratory protective equipment rather than a rating system.
3. The lack of adequate research for investigating all matters relative to civilian respiratory protective equipment.
4. The lack of a formal review of proposed Bureau of Mines approval schedules by industrial hygiene groups.

In every case, the temptation to prescribe the cure for each problem was deliberately avoided, for it is believed that the necessary corrective action requires the organized attention of the industrial hygiene associations rather than the opinions of any individual.

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HYGIENIC GUIDE SERIES

Lead and its Inorganic Compounds

I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours) : 0.2 mg per cubic meter of air.[1]

(1) Basis for Recommendation: Human experience.

B. SEVERITY OF HAZARDS:[2, 7, 11]

(1) Health: Moderate, for brief exposure; high, for prolonged. Lead dust and the dusts and fumes of all but the most insoluble compounds (e.g. sulfide, chromate), are readily absorbed on inhalation, and to a lesser degree after ingestion.[4, 9] Lead and its inorganic compounds are not ordinarily absorbed through the skin. The first detectable clinical result of excessive lead absorption is an increase in the lead content of the urine, followed shortly by an increase in the blood. A rise in the urinary coproporphyrins may subsequently occur. The early symptoms of lead intoxication are most commonly gastrointestinal disorders, colic, constipation, etc. The presence of stippled cells, (except in tetraethyl lead poisoning) followed in time by anemia, may be noted. Weakness, which may go on to paralysis chiefly of the extensor muscles of the wrists and less often of the ankles, is noticeable in the more serious cases. Involvement of the brain (encephalopathy), the most serious result of lead poisoning, is frequently noted in children, but rarely (except from organic lead) in adults.

(2) Fire: None.

C. SHORT EXPOSURE TOLERANCE: Not known quantitatively, but is a factor of *dosage x time*.

D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE: Not known, in cases of inorganic compounds. The minimum lethal dose of a soluble salt, by ingestion, is about 10 gm.

II. Significant Properties

Elementary lead is a dense silvery metal.

Chemical symbol:	Pb
Atomic weight:	207
Specific gravity:	11.34
Melting point:	327°C.
Boiling point:	1613°C.

III. Industrial Hygiene Practice

A. RECOGNITION: Lead and alloys of high lead content are widely employed where properties of softness, high density, low melting point, and resistance to corrosion are needed. Lead is also a common minor component of many bronzes and free-machining steels. Lead compounds are found in paint pigments, ceramics, plastics, insecticides, and storage batteries.

B. EVALUTION OF EXPOSURE:

(1) Direct instrumentation: None available.

(2) Chemical: Collection of fumes or dust with electrostatic precipitator, filter, or impinger, followed by analysis by polarographic, spectrographic, or dithizone procedure.[3, 6]

NOTE: The American Standards Association Z37.11-1943 Standard is being revised. The Subcommittee on Lead of the Z37 Sectional Committee has recommended the adoption of 0.5 mg Pb/M^3 as the maximum acceptable atmospheric concentration for lead chromate and lead sulfide, and 0.2 mg Pb/M^3 for metallic lead and all other inorganic lead compounds.[5]

Mr. Manfred Bowditch (Lead Industries Assoc.), Dr. Harriet L. Hardy (Massachusetts Institute of Technology), and Dr. R. A. Kehoe (University of Cincinnati) assisted the Hygienic Guides Committee in the development of this Guide.

C. RECOMMENDED CONTROL PROCEDURES: Maintain workroom atmospheric concentrations below 0.2 mg/M³. In processes involving melting of metallic lead (such as soldering), dross rather than fume is usually the major problem. Lead fumes will be evolved at red heat temperature. Handle powders of lead compounds in closed systems, or under exhausted hood. Practice good housekeeping and personal hygiene when using lead powders (storage battery plants, paint factories). Grinding and spraying of lead and solder and the spraying of lead paints require good ventilation and/or personal protection for the worker.

IV. Specific Procedures

A. FIRST AID: Usually not important

B. SPECIAL MEDICAL PROCEDURES:

(1) Preplacement examinations. Perform urine and blood analyses for lead.[3, 6] Normal values are:[11]

Urine (spot sample):
0.01–0.12 mg/liter
(sample of large volume):
0.01–0.08 mg/liter
Blood:
0.01–0.06 mg/100 gms.

(2) Periodic examinations (preventive): Perform lead analyses on blood and/or urine.[3, 6] The blood content is the more significant index of absorption, with levels in excess of 0.08 mg Pb/100 gms. of blood (not less than two results obtained by methods having a precision of ± 10 per cent) indicative of excessive absorption and the need for cessation of further exposure. When the blood level approaches 0.08 mg per 100 gms, the employee's exposure should be reduced. This is a reliable index and if properly used, lead intoxication can be completely prevented by modifying the duration and severity of exposure. Urinary values are more variable and therefore, less reliable as an index of excessive exposure, but urine analyses should be made at the same time blood analyses are performed, for maximum medical control, since the average rate of the urinary excretion of a group of comparably employed persons is the best indication of the severity of their current exposure.

(3) Periodic examinations (diagnostic): When clinical symptoms are present, perform urine and blood analyses for lead. It may be desirable to supplement these with coproporphyrin estimation in the urine,[10] and hemoglobin and stippled cell determinations of the blood.

(4) Treatment: Remove immediately all cases of lead intoxication from further exposure until the blood level is reduced to a safe value. Immediately place the individual under medical management and give supportive treatment as indicated. The intravenous administration of the calcium salt of ethylene diaminetetraacetic acid (Ca EDTA; calcium disodium versenate; edathamil, calcium disodium) is of value.[8] However, its use must be rigorously controlled because of harmful effects.

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Ethylene Dibromide

(1,2, Dibromoethane)

I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours): 25 parts of vapor per million parts of air, by volume (ppm).[1]

(1) Basis for Recommendation: Animal studies.[6]

B. SEVERITY OF HAZARDS:

(1) Health: High, for acute; no evidence of cumulative toxicity. Causes irritation of all exposed tissues, respiratory tract, skin and eye. Death can occur from skin absorption. Acute toxicity equivalent to that of carbon tetrachloride or methyl bromide. May produce vesiculation on skin contact and very probably if confined under any skin covering.

(2) Fire: None.

C. SHORT EXPOSURE TOLERANCE: Unknown for man. Cats tolerated a 4-hour exposure of 270 ppm, and guinea pigs a 10-minute exposure of 8600 ppm.[3] The following data are reported by Rowe, et al,[6] for female rats for single inhalation exposures:

Concentration (ppm)	Time without adverse effect (hrs.)	Time with adverse effect (hrs.)
800	0.1	0.15
200	0.7	1.0
100	2.5	4.0
50	7.0	—

D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE: Unknown for man; but 5000 ppm for more than a few minutes might be fatal.

II. Significant Properties

A colorless liquid with an odor resembling that of chloroform.

Chemical formula:	$CH_2BR.CH_2Br$
Molecular weight:	188
Specific gravity:	2.18 (20°/4°C)
Boiling point:	131.7°C
Relative vapor density:	6.5 (air = 1)
Odor threshold:	below 25 ppm
At 25°C. and 760 mm Hg,	
1 ppm vapor:	0.00768 mg/l
1 mg/l vapor:	130 ppm
Solubility:	Water, slight (0.43 parts in 100 parts at 30°C); miscible with alcohol and ether

III. Industrial Hygiene Practice

A. RECOGNITION: Used in fumigants, and in organic syntheses; as a solvent for fats, waxes, celluloid, and oils; and as a constituent of ethyl gasoline, lubricating gasolines and water-proofing preparations.

B. EVALUATION OF EXPOSURES:

(1) Direct instrumentation: Devices are manufactured by Davis Emergency Equipment Co., Newark, N. J. The Fumiscope (Robert J. Hassler Co., Altadena, Calif.) is applicable for measurements above 500 ppm. A halide leak detector (torch) can be used for qualitatively indicating the presence above 45 ppm.

(2) Chemical method:

(a) Determined by passing vapors through quartz tube heated to 950–1000°C, absorbing combustion products in dilute sodium hydroxide, and determining the bromide by the Kolthoff-Yutzy method.[5]

(b) Absorb in ethyl alcohol, decompose with sodium hydroxide, and estimate bromide by Volhard thiocyanate titration.[4]

C. RECOMMENDED CONTROL PROCEDURES: Maintain workroom atmosphere below 25 ppm. This will usually require process ventilation in view of the significant vapor pressure of ethylene dibromide. Containers should be kept closed. Use protective eye equipment. Avoid all skin contact. Most commonly used protective clothing is not satisfactory and may aggravate the skin hazard due to confinement of the liquid or vapor. Neoprene containing 0.5 to 1% nylon is reported satisfactory.[2]

IV. Specific Procedures

A. FIRST AID: Remove exposed indivdual to fresh air. Remove all contaminated clothing. Exposed skin must be washed promptly with an abundance of soap and water. If cyanotic, administer oxygen.

B. SPECIAL MEDICAL PROCEDURES: Keep patient under medical observation for at least 48 hours. Appreciable skin exposure may result in not only inflamed, sensitive areas, but considerable vesiculation. A 48-hour medical observation period for delayed systemic or cutaneous effects is advised.

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Methyl Bromide

I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours): 20 parts of vapor per million parts of air, by volume (ppm).[1]

(1) Basis for Recommendation: Human experience and animal studies.[9]

B. SEVERITY OF HAZARDS:[3, 6, 10]

(1) Health: Acute hazard is high from exposure of lungs, skin and intestinal tract. Repeated exposures to concentrations which singly are asymptomatic may be injurious. Acute effects are primarily to the respiratory tract, with pulmonary edema likely. This, as well as the onset of central nervous system symptoms, may be delayed. They may occur singly or together. Effects may also be produced on the gastrointestinal system, the liver, and the kidneys. Effects may be delayed 48 hours following a single exposure. Overexposure may be fatal. May produce vesiculation on skin contact and very probably if confined under any skin covering. Vapor exposure may produce blistering under covered area.

(2) Fire: None.

C. SHORT EXPOSURE TOLERANCE: Rats and rabbits survived 500 ppm for exposures of 2 and 6 hours, respectively.[3] 600 ppm for several hours may be fatal.[5]

D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE: Fatal to guinea pigs in 5 minutes at 29,000 ppm.[5] 12,850 ppm is 100% fatal to rats and rabbits with respective exposures of six and thirty minutes.[3]

II. Significant Properties

Colorless, nonflammable gas at ordinary temperatures and pressures, with practically no odor

Chemical formula:	CH_3Br
Molecular weight:	95
Boiling point:	4.5°C.
Relative vapor density:	3.28 (air = 1)
At 25°C. and 760 mm Hg,	
1 ppm of vapor:	0.00389 mg/l
1 mg/l of vapor:	257 ppm
Solubility:	Insoluble in water; soluble in most organic solvents.

III. Industrial Hygiene Practice

A. RECOGNITION: Used as a fumigant, refrigerant, and chemical intermediate. Responses vary with concentration. Acute responses are headache, dizziness, nausea, vomiting, and post exposure collapse, followed by fullness of chest, unconsciousness, and respiratory embarrassment. Repeated exposure responses are usually blurred vision, tremors, and staggering gait.

B. EVALUATION OF EXPOSURES:

(1) Direct reading instruments: The Electro Conductivity Analyzer (Davis Emergency Equipment Co., Inc., Newark, N. J.) or the Lira Infrared Gas and Liquid Analyzer (Mine Safety Appliances Co., Pittsburgh, Pa.) may be used. A halide

leak detector may be used for concentrations above 25 ppm, while the Gow Mac Gas Meter (Gow Mac Instrument Co., Madison, N. J.) has applications above 500 ppm.

(2) Chemical method: Determined by passing through quartz tube heated to 950–1000°C., absorbing combustion products in dilute NaOH and determining the bromide by the Kolthoff-Yutzy method,[4] or potentiometrically.[7]

C. RECOMMENDED PROCEDURES: Maintain air concentrations below 20 ppm. Avoid all skin contact. If protective clothing is used, confinement of liquid or vapor beneath it must be prevented. Respirators or gas masks approved by the U. S. Bureau of Mines for organic vapors are useful for temporary exposures. When used as a fumigant, no parts of the building should be occupied unless rigid precautions are taken to prevent leakage into inhabitated areas.

IV. Specific Procedures

A. FIRST AID: Remove individual to fresh air. Remove all contaminated garments. Skin may be washed with bicarbonate of soda solution. Keep patient under medical observation for at least 48 hours. If cyanotic, administer oxygen.

B. SPECIAL MEDICAL PROCEDURES: Convulsions may be controlled by barbiturates. If pulmonary edema develops, prompt bed rest, accompanied by administration of 100% oxygen, should be established. If liver is enlarged or if there is epigastric pain, the administration of glucose intravenously may be indicated, but only if there is no risk of pulmonary edema.

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Uranium (Natural)

I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours):

Authority [a]	μc/ml [b]	d/m/M³ [c]	μg/M³ [d]
NBS[10]	5.1×10^{-11}	110	78
Part 20[2]			
Adults	5×10^{-11}	110	75
Minors	1.7×10^{-12}	4	2.6
ICRP[8]	9×10^{-11}	400	270
ACGIH[1]			
Soluble compounds	—	—	50
Insoluble compounds	—	—	250

Note:

a. NBS: National Bureau of Standards. Part 20: Code of Federal Register, Part 20.
ICRP: International Commission for Radiation Protection.
ACGIH: American Conference of Governmental Industrial Hygienists.

b. μc/ml: microcuries per milliliter of air.

c. d/m/M³: disintegrations per minute per cubic meter of air.

d. μg/M³: micrograms per cubic meter of air.

(1) Basis for Recommendation: The threshold limit for soluble materials was derived from chemical toxicity studies on animals.[11] Permissible limits for insoluble materials have been derived from calculations

based on a maximum irradiation level of 300 mrem/week to the critical organ (lung).[9] A maximum level of 10 mg U/liter of water has been established for public drinking water supply.[2]

B. SEVERITY OF HAZARDS:

(1) Health: High, for both chronic and acute—probably as toxic as mercury or lead.[11] Soluble compounds affect the kidney; insoluble, the lung. No significant warning properties. Insoluble compounds are slowly removed from the lung, and since they are alpha emitters, may be internal radiation hazards. Moderate hazard to skin from direct contact for prolonged periods.

(2) Fire: Servere. Uranium is pyrophoric and reacts with carbon dioxide.[7] A dust cloud of the metal will ignite violently at room temperature. Ignition temperature of a dust smaller than 270 mesh is only 20°C. The explosive concentration is 0.060 oz/ft^3, or 60 gms/M^3. [5]

C. SHORT EXPOSURE TOLERANCE: Using insoluble compounds, 80,000 μg/M^3 produced histological changes in experimental animals. 10,000 μg/M^3 produced no changes.[6] With soluble compounds, 200 μg/M^3 for one year produced slight injury, while 50 μg/M^3 produced no injury and mild histological damage to a few.[7] Similar exposures of humans have produced no measurable abnormalities.

D. ATMOSPHERIC CONCENTRATIONS IMMEDIATELY HAZARDOUS TO LIFE: Unknown for man. Accidental exposure of a few seconds to high concentrations of a mixture of soluble uranium (UF_6 and UO_2F_2) and hydrogen fluoride resulted in death within minutes.[11] No reported cases of chronic uranium toxicity for humans.

II. Significant Properties

A dark grey, heavy metal, ductile and malleable. Composed of three isotopes: U-238 (99.28%), U-235 (0.715%), U-234 (0.005%). Oxidizes rapidly in air, with formation of oxide film of U_3O_8. Chip uranium burns quietly in air, forming U_3O_8.

Chemical symbol:	U
Atomic weight:	238
Specific gravity:	18.7
Melting point:	1150°C.
Radiation emitted:	alpha, beta, gamma
Specific activity:	
1.5 tons:	1 curie
1 μg:	1.4 d/m (alpha)
1 μg (fully enriched:	~ 150 d/m (alpha)
Surface dose rate:	200–240 m rad/hr (beta)
(equilibrium with UX, and UX_2):	~ 2 mr/hr (gamma)

III. Industrial Hygiene Practice

A. RECOGNITION: Major use is as nuclear reactor fuel. Various operations produce dust, fume, or mist exposures.

B. EVALUATION OF EXPOSURES:

(1) Air sampling by collection on filters.

(2) Chemical methods:

(a) Colorimetric determination using ferrocyanides developed by Cohenour and Davis.[11]

(3) Radiometric: Alpha counting procedures.[3]

C. RECOMMENDED CONTROL PROCEDURES: Maintain workroom exposures below acceptable limits, using adequate ventilation. Local ventilation is usually necessary.[4] Direct skin contact should be limited to about 6 hrs./wk. The use of leather palmed gloves provide sufficient shielding to permit 4–6 times this contact period.

IV. Specific Procedures

A. FIRST AID: (acute exposures of soluble compounds only). Remove from exposure, place at bed rest, call physician.

B. SPECIAL MEDICAL PROCEDURES: Any person with a known kidney disorder should be considered unsuitable for work with uranium. Urinary uranium is determined by fluorimetry.[3] Permissible levels vary with different organizations from a low of 5 μg/l to about 100 μg/l. Urinalysis is not recommended as a sole criterion for excessive exposure.

V. Literature References

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Silica

(Amorphous)

I. Hygienic Standards

A. SUGGESTED MAXIMUM ATMOSPHERIC CONCENTRATION: Unknown. May vary with origin of product and particle size. 20 million particles per cubic foot of air (MPPCF) has been suggested for amorphous diatomite.[1, 9]

B. SEVERITY OF HAZARDS:

(1) Health: Only a limited amount of information exists on the physiological effects of amorphous silica dust, with a difference of opinion as to whether or not it will cause lung damage. Chest x-rays of persons exposed to natural diatomite dust for as many as 30 years indicated only a fine granular pattern or a linear exaggeration, with no coalescent lesions. Other reports indicate the occurrence of severe pneumoconiosis with relatively short exposures to diatomaceous earth.[7, 8] It is probable that the reported cases resulted from the calcined rather than the natural product. Persons exposed to tripoli dust for 8 years showed no alterations in lung markings, no reduction of vital capacity, nor any effects on general health.[4] The results of recent animal experiments with submicron particles of amorphous silica are of uncertain significance, in some cases producing a fibrotic reaction,[5] and in others a cellular type of response.[6] Further work appears necessary to evaluate the effects of this type of dust.

(2) Fire: None.

C. SHORT EXPOSURE TOLERANCE: High level exposures, even though brief and intermittent, should be avoided.[1, 9]

D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE: Not applicable.

II. Significant Properties

Amorphous silica is contained in siliceous deposits variously termed diatomite, diatomaceous earth, infusorial earth, kieselguhr and tripolite. The silica content varies with the different forms of material. Synthetic products, of submicron size particles, are available under the following trade names: Aerosil, Cab-O-Sil, Fransil, HiSil, Ludox, Santocel, Quso, Syton, and Syloid.

Chemical formula: SiO_2

Molecular weight: 60

III. Industrial Hygiene Practices

A. RECOGNITION: Industrial uses are: filter aids, extenders, flatteners, polishers, liquid absorbers, and high temperature insulation.

B. EVALUATION OF EXPOSURES: Microscopic amorphous silica dust may be sampled with the electrostatic precipitator or by the impinger method, using alcohol or alcohol and water as the collecting medium, and dust counts made up by the standard light field technique.[2] Satisfactory methods for evaluating exposures resulting from the submicron materials have not been devised, although methods based upon weight or upon electron photomicrography[3] seem most logical.

C. RECOMMENDED CONTROL PROCEDURES: To prevent exposure to high concentrations of amorphous silica dust, process ventilation and/or enclosure are the best means of control. For some operations a dust respirator approved by the U. S. Bureau of Mines may be satisfactory.

IV. Specific Procedures

A. FIRST AID: None.

B. SPECIAL MEDICAL PROCEDURES:

(1) Preplacement: Clinical and chest radiographic examinations should be made on all persons prior to job assignment.

(2) Periodic: Since there is only limited information about the harmful effects of amorphous silica in industry, exposed personnel should have careful periodic medical examinations, including chest x-ray. Pulmonary function testing may be useful.

(3) Treatment: No satisfactory treatment other than removal from exposure, and therapy for any complicating infection.

V. Literature References

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9. U. S. Public Health Service; California Department of Public Health; Nevada State Health Department; Oregon State Board of Health: Progress Report of Study of Pneumoconiosis Hazards in the Diatomite Processing Industry. 1955.

Asbestos

I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours): 5 million particles per cubic foot of air (MPPCF).[1]

(1) Basis for Recommendation: Experience in industry,[2, 4, 8, 12, 13] and animal experiments.[5, 7]

B. SEVERITY OF HAZARDS:

(1) Health: Long continued inhalation of asbestos dust results in a form of pneumoconiosis known as asbestosis. The primary effect of inhalation is an interstitial pulmonary fibrosis. The disease is characterized by asbestos bodies in the lungs and sputum. Based on roentgenological examinations, asbestosis can be classified as minimal, moderate, and advanced. It is a serious disease in some instances, but more frequently it remains nondisabling for many years, even without appreciable symptoms, as long as some other serious disease does not supervene to cause death.[2] Chief symptoms of advanced asbestosis are variable cough, dyspnea, substernal chest pains, decreased chest expansion, weakness, emaciation, clubbed finger tips, and curved fingernails. Any appreciable decrease in the amount of asbestos dust in the breathing atmosphere will cause a decrease in the incidence and severity of asbestosis. Individual suceptibility varies.[8] There have been reports of an increased incidence of lung cancer in persons with asbestosis.[3]

(2) Fire: None.

C. SHORT EXPOSURE TOLERANCE: Not applicable:

II. Significant Properties

A fibrous magnesium calcium silicate which occurs in various combinations as white, greyish or greenish masses, either compact or of long silky fibers, flax-like and readily separated. About 95% of commerical asbestos is chrysotile, which is derived from serpentine, and is a hydrous magnesium

silicate containing from 12 to 14 per cent water of crystallization.

III. Industrial Hygiene Practice

A. RECOGNITION: The spinning and weaving of asbestos, in combination with other textiles for fire proof and heat resistant cloth, results in dust exposure. It may be used by itself or combined with other materials for valve packings, gaskets, boiler lagging and pipe covering, protective clothing, shielding materials, and as automotive brake linings. In the building industry it is used in the manufacture of asbestos cement products, heat insulating, and fireproofing materials.

B. EVALUATION OF EXPOSURES: Asbestos dust may be sampled with the electrostatic precipitator or by the impinger methed using alcohol or alcohol and water, as the collecting medium,[4, 6] and dust counts made by the standard light field technique.[5] The recommended maximum atmospheric concentration of 5 MPPCF is based upon the impinger sampling procedure.

C. RECOMMENDED CONTROL PROCEDURES: Prevention of asbestosis depends entirely upon preventing exposure to concentrations of dust sufficiently high to produce the characteristic reaction. Enclosure or local exhaust ventilation are the principal means of dust control. U. S. Bureau of Mines approved dust respirators may be worn as protection for some operations.

IV. Specific Procedures

A. FIRST AID: None.

B. SPECIAL MEDICAL PROCEDURES:

(1) Preplacement: Clinical and radiographic chest examinations prior to job assignment.

(2) Periodic: Exposed personnel should have periodic clinical examinations for signs and symptoms of asbestosis. These should include examination of the sputum for asbestosis bodies, and chest x-rays of good quality.

(3) Treatment: No satisfactory treatment other than removal from exposure and therapy for any complicating infection.

V. Literature References

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3. Doll, R.: *Brit. J. Ind. Med., 12:* 8, 1955.
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Because of space limitations, it is impossible to list all methods of exposure evaluation. The selections have been made on the basis of current usage, reliability, and applicability to the usual industrial type of exposure. Any specific evaluation and/or control problem will involve professional judgment. This can best be done by professional industrial hygiene personnel.

Respiratory protective devices are commercially available. Their use, however, should be confined to emergency or intermittent exposures and not relied upon as primary means of hazard control.

A relative scale is used for rating the severity of hazards: nil, low, moderate, high, and extra hazardous.

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News of Local Sections

Chicago

Mr. Albert Edwards, formerly industrial hygienist for the Portland Cement Association, joined the staff of the Division of Industrial Hygiene, Indiana State Board of Health, March 1st.

Mr. Clark Bridges has been named Assisting Manager Director of the Industrial Medical Association with headquarters at 28 E. Jackson Blvd., Chicago. He assumed this newly created position on January 1st, after serving three and one-half years as Assistant Secretary, Council on Industrial Health of the American Medical Association.

Dr. F. A. Van Atta, Industrial Hygienist, United Automobile, Aircraft and Agricultural Implement Workers of America, was our February speaker. Floyd, although now located in Detroit, is still a member of our Chicago Section. His topic was—"An Industrial Hygienist in a Labor Organization," and he discussed the educational work he is doing with many Union Locals.

Our March meeting program was called "Problem Night." Prior to and at the meeting members were invited to submit industrial hygiene problems for discussion by a panel. The moderator was Dr. Paul J. Whitaker, Medical Director, Allis-Chalmers Mfg. Co., and other panel members were Howard Schulz, American Medical Association, Dr. Eugene Walsh, Medical Director, International Harvester, and Herbert Walworth, Lumbermen's Mutual Casualty Company. Many of the members helpfully participated in the discussion of problems presented.

Western New York

At our meeting, on March 5th, officers for the 1958–1959 year were installed. They are—President, Mr. Franklin A. Miller; President-Elect, Mr. Herbert I. Miller, Jr.; Secretary-Treasurer, Mr. Richard F. Scherberger; Directors, Sanford Hartwell, Paul Morrow and C. Wilson McMath. After our business meeting, an extremely interesting discussion of Operation Plumb Bob at the Nevada testing grounds was given by the project director, Dr. J. Newell Stannard, and the two assistant directors, Mr. Robert Wilson and Dr. Robert Thomas. Operation Plumb Bob was concerned with simulating a possible nuclear disaster such as might occur in a crash involving a vehicle bearing a nuclear device.

Northern California

At our meeting on January 28th, officers for the coming year were nominated as follows: President-Elect, Robert J. Owens; Secretary-Treasurer, Henry R. James; Elective Committee (3 years), William J. Wolf. After the business meeting we listened to an interesting and informative talk by Francis R. Holden, Ph.D., on "Radiation Protection—Present Day Practical Problems."

Southern California

Jack Rogers, Engineering Director, and Harold Price, M.D., Medical Director, Division of Occupational Health, Los Angeles, talked to us on "Engineering and Medical Aspects of the Industrial Hygiene Problems in the Field of Plastics." They brought out that sensitization is a major problem encountered in the plastics industry.

At our meeting on March 13th, a panel discussed "Trends in Workmen's Compensation." Panel members were L. C. Chase, moderator R. T. Johnstone, M.D., and D. A. Campbell.

Detroit

The Michigan Industrial Hygiene Society (Detroit Section AIHA) elected officers for 1958–59. V. J. Castrop was elected president-elect and D. L. Eschelbach was elected secretary-treasurer. J. V. Brasch, H. E. Jaworski, W. McNab and Dr. D. J. Wood were elected to the Executive Committee serving with R. S. Ajemian, P. M. Giever, M. Schuman and Dr. A. Vorwald whose terms of office continue. W. A. Cook succeeds to the presidency replacing P. E. Toth who retires to the past-president office.

Dr. C. R. Williams, president of AIHA, was the speaker for the dinner meeting held on February 13. His subject was "Recent Occupational Health Exposures."

Dr. F. A. Van Atta, who recently joined the UAW-CIO as industrial hygienist, spoke at the March 11, dinner meeting. His subject was "Functions of an Industrial Hygienist in a Labor Union."

An all day meeting has been planned for May 20. The program will include papers on several subjects of current interest. This meeting will be held at the General Motors Technical Center in Warren, northeast of Detroit.